EVALUATION OF HIGH-TEMPERATURE RESINS IN ASBESTOS FIBER REINFORCED LAMINATES

M. B. Smith

WHITTAKER CORPORATION

Narmco Research & Development Division

TECHNICAL REPORT AFML-TR-67-389

March 1968

Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

93

NOTICES

When US Government drawings, specifications, or other data are used for
any purpose other than a definitely related Government procurement operation,
the Government thereby incurs no responsibility nor any obligation whatsoever;
and the fact that the Government may have formulated, furnished, or in any way
supplied the said drawings, specifications, or other data, is not to be regarded
by implication or otherwise, as in any manner licensing the holder or any other
person or corporation, or conveying any rights or permission to manufacture,
use, or sell any patented invention that may be related thereto in any way.

This document is subject to special export controls and each transmittal
to foreign governments or foreign nationals may be made only with prior approval
of the Air Force Materials Laboratory (MAAE), Wright-Patterson AFB, Ohio 45433.

Copies of this report should not be returned unless return is required by
security considerations, contractual obligations, or notice on a specific
document.

EVALUATION OF HIGH-TEMPERATURE RESINS
IN ASBESTOS FIBER REINFORCED LAMINATES

M. B. Smith

FOREWORD

This report was prepared by Whittaker Corporation, Narmco Research & Development Division, San Diego, California, under Contract AF 33(615)-5071, "Characterization of High-Temperature Polyimide Resin in Asbestos Fiber Reinforced Laminates." This contract was initiated under Project Nr 7381, "Materials Application," Task Nr 738106, "Design Information Development," BPSN 66(687381-738106-62405514). Work was conducted under the administration of Mr. Weldon Scardino, MAAE, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

This report covers the period from 1 September 1966 through 1 October 1967. The manuscript was released by the author in November 1967 for publication as a technical report.

Mr. M. B. Smith, Narmco Senior Engineer, was in charge of this program. Others who cooperated in the planning and research of this program were Mr. B. Levenetz, Assistant Engineering Department Manager; Mr. R. Gill, Statistician; and Mr. A. Wignall, Senior Technician.

Many of the items compared in this report are commercial items that were not developed or manufactured to withstand the tests to which they were subjected or to operate as applied during this program. Any failure to meet the objectives of this study is no reflection on any of the commercial items discussed herein or on any manufacturer.

This technical report has been reviewed and is approved.

ALBERT OLEVITCH, Chief
Materials Engineering Branch
Materials Application Division
Air Force Materials Laboratory

ii

ABSTRACT

This work involved an evaluation of the usefulness of epoxy and polyimide in asbestos paper or asbestos mat reinforced laminates. Initially, a crocidolite asbestos mat laminated with a polyimide resin was considered a good candidate, but process optimization studies failed to raise flexural strengths above the 20,000-30,000 psi level. The problem appeared to be one of inadequate wetting of the asbestos fibers, in combination with the excessive volatiles now inherent in the polyimide system itself. Fundamental studies later pointed out the asbestos fibers are very sensitive to buckling, and that voids in the resin matrix cannot be tolerated. Hydroclaving at 30,000 psi was also used in an attempt to alleviate this problem. Eventually, however, it was found that dilute methyl ethyl ketone solutions of epoxy resins — which do not develop volatiles and the consequent voids — provided the best impregnation. Crocidolite and epoxy composites were optimized at about 25 weight percent resin, 2.4 g/cc specific gravity, and 1.5 (or less) volume percent void content. Processing pressures of 1000-5000 psi were required. Long fibers proved to be better than short fibers, and oriented fiber was found to be better than random fiber. By employing the optimized processing conditions, a commercial parallel-fiber crocidolite felt combined with a high-temperature epoxy resin displayed flexural stregnths of 96,000 psi, compressive strengths of 68,800 psi, and tensile strengths of 61,300 psi. Respective modulus values were 9.30, 9.63, and 10.39 $\times$ 10^6 psi. In general, a parallel-fiber crocidolite laminate incorporating polyimide resin failed to provide respectable results, even when the optimized processing conditions were used.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF ILLUSTRATIONS

LIST OF TABLES

INTRODUCTION

PROGRAM DIRECTION

The objective of this program was to evaluate the usefulness of the newer polyaromatic polymers in reinforced flat laminates. Work involved developing and optimizing fabrication and processing procedures for these composites, with an ultimate goal being the generation of preliminary mechanical properties data. Resistance to extended exposure at elevated temperatures was also a target.

Before any work commenced on the program, efforts were redirected from the originally proposed AF-R-151 polybenzimidazole polymer with 1581 style HTS S-glass reinforcement to the N-arylene benzimidazole polymer with asbestos reinforcement. This was a logical decision, since several advantages of the newer polymer were indicated. The decision to replace glass with asbestos was intended to eliminate duplication of effort being conducted on an allied Air Force sponsored program.

Work with these materials was begun within the original framework of the contract. Because of reduced material costs, several approved added tasks were undertaken, including basic polymer studies such as polymerization rate and volatiles determinations of the new N-arylene benzimidazole, plus asbestos reinforcement, screening, and initial prepreg studies. A list of sequential statistically designed experiments for conducting the process development phases of the program was drawn up and was approved.

Although the basic polymer studies were completed and reinforcement screening begun (see Table I), it became apparent that the polymer was advancing too rapidly in the presence of its m-cresol solvent, even when stored for short periods of time (1 week) at 0°F. This instability was also evidenced by increasingly poor spreadability during impregnation of reinforcement material, accompanied by poor mechanical properties of glass fabric laminates used for quality assurance purposes (Table I, comparing systems 2 and 3). Rather than continue work with a system whose unsuitability for this application was by now obvious, the decision was made to look for a resin binder replacement.

Initial probing indicated that polyimide resin might be a good substitute for the N-arylene-benzimidazole. Skybond 700 polyimide, a product of Monsanto Company, appeared to be the best choice since it is available in solution form and therefore would afford good saturation of the asbestos. Furthermore, it can be processed at comparatively low pressures (vacuum bag) and temperatures (350°F), which makes it adaptable to production. A final argument in favor of this resin system was that information on polyimide-asbestos composites would round out the Air Force's accumulation of important polyimide engineering data.

TABLE I

TYPICAL MECHANICAL PROPERTIES OF LAMINATING SYSTEMS
CONTROLLING CHOICE OF RESIN USED ON THIS PROGRAM

Laminating Systems	Flexural Strength (psi) and Modulus (psix10⁶)									
	RT Initial		600°F Initial		600°F after 100 hr @ 600°F in Air		600°F after 200 hr @ 600°F in Air		600°F after 300 hr @ 600°F in Air	
AF-R-151 benzimidazole polymer/1581 S-glass, HTS finish	99,600	3.92	92,860	3.62	12,820	0.75	2,480	0.88	--	--
N-arylene benzimidazole polymer/1581 S-glass, HTS finish, original data, m-cresol solvent	40,000	--	--	--	48,600	--	--	--	54,000	--
N-arylene benzimidazole polymer/1581 S-glass, scaled-up data, m-cresol solvent (Unstable in solvent)	38,800	2.56	30,200	1.69	--*	--	--*	--	--*	--

* Burned out.

PROGRAM PLAN OF SEQUENTIAL STATISTICALLY DESIGNED EXPERIMENTS

Asbestos Reinforcement Studies

A study was initiated to determine the type of asbestos mat that would impart good mechanical properties to laminates exposed to extended heat aging at elevated temperatures.

Eight asbestos mat types were selected from the numerous types available on the market (see Table II). These selections embodied the best types available for the present application, and included thickness, type, and finish parameters. One laminate was made with each type, using the input from the previous polymerization/volatiles and prepregging studies. In general, type selection was initially the most important aspect of the study, because thickness would be determined by what could be successfully coated and prepregged. Need for finish was also an important consideration and was studied subsequently. Eight types of asbestos mat were prepregged and laminates prepared from each by press lamination. All process variables were held constant to afford response from the type of mat.

Statistical analysis of the preceding study was carried out by a simple comparison of means at the 99% one-sided confidence level of the t statistics. Based on previous flexure data available from the IMIDITE 1850/1581 system, it was estimated that sample variances from individual laminates could be as high as approximately 10 ksi. Using this as an estimate of expected variances from the eight selected asbestos reinforcements, it was proposed that 12 replicates be tested in flexure after 200-hour heat aging at 600°F in air for comparison purposes. With 12 replicates at the 99% confidence level, the sensitivity of the test would result in a detectable difference of the means at approximately 8 ksi.

$$\frac{t_{0.01}s}{\sqrt{n}} = \frac{(2.7)\ (10)}{\sqrt{12}} = 8\ \text{ksi}$$

2

TABLE II

CANDIDATE MATERIALS FOR ASBESTOS SCREENING

Material (Manufacturer)	Thickness, mils	Binder	Type Asbestos	Glass
PYROTEX 40 RPD (Raybestos-Manhattan)	10	RB6	Chrysotile	1% scrim cloth
PYROTEX 70 RPD (Raybestos-Manhattan)	10	None		---
NOVABESTOS 7301 (Raybestos-Manhattan)	5	None		---
NOVABESTOS 7311 (Raybestos-Manhattan)	10	None		60%-65%
C10-G15 Mat (Amercoat Corp.)	20	5-7%	Crocidolite	---
BLUE PAPER (W. M. Schulz Co.)	10	Buna N		---
PAPER "F" (Johns-Manville)	10	None	Chrysotile	---
MICROBESTOS "A" (Johns-Manville)	10	None		Unidirectional glass threads

After screening was accomplished, selection of the most suitable reinforcement, additional evaluation of this particular reinforcement, and investigation of finish and/or binder, was carried out using a simple factorially designed experiment. Design necessitated fabrication of one or two additional laminates, thus restricting this whole phase to a maximum of 10 laminates.

Optimization of the Skybond 700 Polyimide and Selected Asbestos Reinforcement System

The following variables introduced in the lamination process prior to initiation of the cure cycle were assumed constant within the ability of stringent process and materials control:

1. Skybond 700

2. Selected asbestos mat

3. Prepreg method

4. Prepreg resin content

5. B-stage time and temperature

Small variations in these process "constants" were accepted as part of the experimental error in subsequent factorial design analysis of variance. Items 3 through 5 above were assumed to be optimized at the outset as a result of work

3

completed in previous sections. Variations in Items 1 and 2 were controlled through batch blending and stringent inspection amd materials handling control, respectively.

Optimization of processing at this point, then, was concerned entirely with cure cycle variables. By reasoning on the basis of physical behavior of materials, the number of important controllable variables during subsequent autoclave type processing was logically reduced to two:

1. Rate of temperature rise

2. Pressure application temperature

With both of these variables obviously independent, other variables such as percent resin, void content, density, and percent flow were a direct function of them. Optimization of the cure cycle was carried out using the response surface — path of steepest ascent methods described in detail in the literature.*

The response function can be written:

$$N = B_0 + B_1 x_1 + B_2 x_2 + \text{higher order terms}$$

where

N is the response surface (e.g., flexural strength after aging, laminate density, void content, resin content, etc.)

x_1 is the rate of temperature rise ($2°$-$20°$F/minute)

x_2 is the pressure application temperature ($300°$-$700°$F)

The path of steepest ascent was determined sequentially be a series of experiments starting at an arbitrary point (P), defined by (x_1) and (x_2) known to produce an acceptable laminate. A half-replicate (2^2) factorial design utilizing upper and lower levels of the two independent processing variables was constructed. The resulting observation responses (N_1) and (N_2) were then used to estimate by the method of least squares the coefficients (B_1) and (B_2) as the slopes of the response surface (plane) in the area of (P).

A second set of laminates was then made at a point removed from (P) along the direction of the steepest response. In this way, step by step, the most rapid approach to a stationary response to process variables was made. Further exploration of the response surface was made at this point to establish whether or not a true maximum has been reached or merely a point of stationary response removed from the maximum. It was established that the fabrication of 50 laminates was required for this phase.

---

* George E. P. Box et al., The Design and Analysis of Industrial Experiments, O. L. Davies, editor, second edition, chapter 11, Hafner Publishing Company, New York, 1956.

4

Amercoat C10-G15 crocidolite asbestos mat was selected as the best of eight asbestos reinforcement materials. When laminated with Skybond 700 in accordance with processing conditions suggested by Monsanto, this material retained as much as 67.8% of the initial room temperature flexural strength after 1 hour at 600°F when tested at 600°F, and as much as 74.3% after 100 hours when tested at 600°F. (The increase was attributed to postcure effects.) Good thermal stability and oxidation resistance at 600°F appeared to be inherent in the system.

Process optimization studies carried out did not give the expected improvement in laminate mechanical properties. Ultimate flexural strength could not be raised above a 20,000-30,000 psi range with Skybond 700. Reinforcement and resin testing verified that these materials were of adequate quality.

Analysis of existing data failed to yield an answer for upgrading marginal mechanical properties; consequently, broad screening of process variables was begun. The use of dry ply in combination with prepreg raised the flexural strength somewhat (32,600 psi), indicating that venting and volatile release may be an influencing factor. Using a dry powder polyimide (DuPont 8122) and poor impregnation procedures, the flexural strength was raised to 42,000 psi. The problem appeared to be associated with the proper or adequate wetting of the asbestos fibers by the resin, and with the inherent characteristics of the polyimide resin.

PROGRAM REDIRECTION TO FUNDAMENTAL ASBESTOS STUDIES

In view of the potential of asbestos as a reinforcing agent (ultimate tensile strength of 469,000-605,000 psi, with a maximum of 1,000,000 psi for crocidolite asbestos, and a reported modulus of elasticity of at least 27.1×10^6 psi), additional and more fundamental studies were undertaken in the area of process optimization to provide a better understanding of the processing required to overcome problems in wetting asbestos by the resin. The high degree of surface activity of the asbestos appeared to be a difficulty, and the following studies were performed prior to proceeding further with lamination studies. To reduce the variables involved, an epoxy-resin was used with crocidolite asbestos. Crocidolite was chosen because of its superior physical properties.

Asbestos Fiber Classification

Suitable techniques were employed for classifying the virgin crocidolite fibers into various grades of fiber length and/or openness and residue of fines. Fluidized bed, specific gravity, vacuum carding, temperature and pressure expansion, and other techniques were utilized. Fiber was classified by the following categories:

1. Very large length-to-diameter (L/D) ratios obtained from unopened asbestos ore or from rock representing long, undamaged fibers.

2. Very small L/D ratios from chopped fibers.

3. Unopened asbestos long fibers as they occur in nature, similar to item 1 above.

4. Highly opened short fibers from chopping, as in item 2 above.

5. Highly opened long fibers by expansion opening, as in item 1 above.

The resultant classified fibers subsequently became candidates for composite specimen preparation and evaluation.

Asbestos Fiber Orientation

Various techniques for unidirectionally orienting asbestos fibers were evaluated in an attempt to maximize the utilization of reinforcement strength in composites. Included were magnetic fields and electrostatic charges, suitable carding techniques, extrusion alignment of resin/fiber mixture, and other techniques.

Asbestos Fiber Surface Studies

Consideration was given to gas absorptiometric techniques and methods to remove chemically absorbed gases prior to resin impregnation. Attempts were made to alter the comparatively nonpolar crocidolite surface by suitable coupling agents such as silanes to enhance the wetability and bonding of the fibers.

Epoxy Resin Matrix

A high temperature epoxy resin was selected, DEN 438 cured with methyl nadic anhydride and DMP-30 accelerator.

Impregnation, B-Staging and Curing Process Studies

In addition to the conventional approaches, newer processing techniques such as hydroclaving (30,000 psi), ultrasonics, and centrifugal methods were investigated as means to enforce rigorous contact and saturation. Infrared, induction, and radiofrequency heating were considered for polymerization.

Compression Specimens and Evaluation

A compression test was used to evaluate the resultant composites in compression to those made with nonreinforced resin. Specimen design conformed with Federal Test Method Standard 406, Method 1021 (1/8 $\times$ 1/2 $\times$ 3 in.) for laminated specimens and ASTM-D-695 (1/2 $\times$ 1/2 $\times$ 1 in.) for molded specimens. Other configurations were considered as required. Test conditions were limited to ambient temperatures (75°F) to expedite screening and to hold costs at a minimum.

Certain joint efforts between Narmco and outside concerns were conducted to find new approaches to the asbestos and polyimide materials and processing problems. Monsanto laboratories at Springfield, Massachusetts prepregged crocidolite mat with Skybond 700, laminated specimens, and reported mechanical properties for comparison with Narmco data. Raybestos-Manhattan, at Bridgeport, Connecticut, reported mechanical properties for laminates made with their first commercial asbestos polyimide prepreg material.

6

PROGRAM AIDS

Planning on this program was influenced heavily by the literature, particularly the literature for asbestos composites dating from 1960 to the present. At this writing, the bibliography for this report is considered to be the most complete document of its kind available. A computerized DDC Report Bibliography (Search Control No. 077645) was included in the literature research effort.

SECTION II

ASBESTOS REINFORCEMENT SELECTION

MATERIALS SCREENING

Eight Skybond 700 polyimide laminates were made with eight candidate asbestos reinforcement materials. The resin impregnation, B-staging conditions, and lamination procedures were similar to those suggested by the manufacturer and are listed in Table III. Room temperature flexural strength and modulus values are listed in Table IV. No attempt was made to optimize the processing for these laminates. The room temperature test condition was selected on the basis of test reproducibility; an elevated temperature factor was included by virtue of the 700°F postcure condition to which every laminate was subjected. Resin impregnation, B-staging, and laminate processing were identical in all cases. See Table III and Figure 1.

TABLE III

MATERIALS SCREENING; SELECTION OF ASBESTOS REINFORCEMENT
MATERIAL FOR SKYBOND 700 FLAT LAMINATES

Laminate No.	Asbestos Reinforcement	No. Plies	% Pickup	% Volatile Content	% Flow	% Resin (Calculated)	Sp Gr	Mils/Ply	Vol % Void Content	% Resin Burnout
1055	Raybestos-Manhattan Pyrotex 40 rpd, 10 mil, 0.0724 g/in.^{2}, binder RB6 (Chrysotile)	15	66.1	16.4	58.0	41.8	1.57	5.1	27.3	43.4
1056	Raybestos-Manhattan Pyrotex 70 rpd, 10 mil, 0.0634 g/in.^{2}, no binder, 1% glass skrim (Chrysotile)	15	71.4	18.5	60.6	27.4	1.69	3.26	31.6	27.8
1057	Raybestos-Manhattan Novabestos 7301, 5 mil 0.0369 g/in.^{2}, pyrolyzed, no glass (Chrysotile)	25	70.9	17.5	46.3	49.5	1.72	2.92	18.4	46.3
1058	Raybestos-Manhattan Novabestos 7311, 10 mil, 0.0483 g/in.^{2}, pyrolyzed, 60%-65% glass (Chrysotile)	15	77.9	20.8	49.6	51.9	1.61	4.0	20.0	52.4
1059	Amercoat C10-G15 mat, 20 mil, 0.1808 g/in.^{2}, no glass, 5%-7% binder (Crocidolite)	10	67.7	20.2	55.2	27.68	1.70	9.0	31.3	27.6
1060	Schulz Blue Paper 10 mil, 0.0956 g/in.^{2}, no glass, Buna N binder (Crocidolite)	15	61.0	14.3	32.2	42.6	1.79	6.0	20.2	38.8
1061	Johns-Manville "F" Paper, 10 mil, 0.1288 g/in.^{2}, 100% inorganic (Chrysotile)	15	44.3	12.1	6.23	40.6	1.72	8.0	22.0	40.8
1062	Johns-Manville Microbestos "A", 10 mil, 0.0913 g/in.^{2}, (Chrysotile)	15	50.3	9.81	5.58	47.6	1.60	6.6	22.0	49.2

NOTE: Laminate Size: 9 in. × 9 in.
    B-Staging: 25 minutes @ 250°F.
    Press Curing: Two 2-ply TFE 30/116 barrier plus four plies 1500 style glass fabric breather on each side. 30 minutes @ 350°F, @ 500 psi, in hot, out cold.
    Postcuring: 2 hours each @ 392°F, 437°F, 482°F, 572°F, 617°F, and 662°F, plus 4 hours @ 700°F in an air-circulating oven
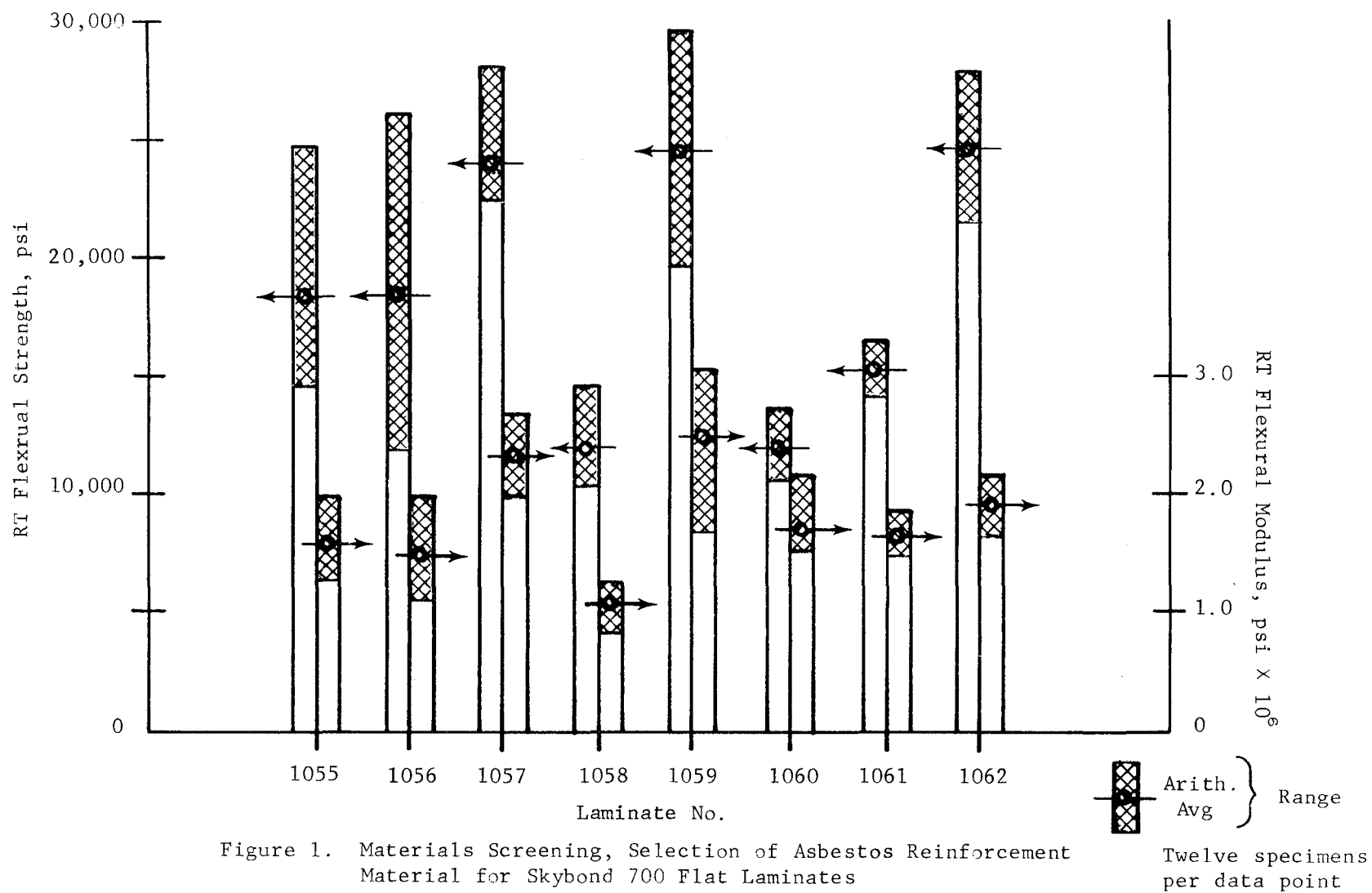
Figure 1.   Materials Screening, Selection of Asbestos Reinforcement
            Material for Skybond 700 Flat Laminates

TABLE IV

ROOM TEMPERATURE FLEXURAL STRENGTH AND MODULUS VALUES
FOR SKYBOND 700 FLAT LAMINATES

RT Flexural Strength (psi) and Flexural Modulus (psi $\times 10^6$)															
Laminate 1055		Laminate 1056		Laminate 1057		Laminate 1058		Laminate 1059		Laminate 1060		Laminate 1061		Laminate 1062	
24,900	1.84	16,500	1.18	23,100	2.22	14,500	1.27	27,100	2.82	12,900	2.19	14,300	1.54	23,300	1.81
21,000	1.60	12,000	1.09	23,000	2.32	11,900	1.12	21,400	2.40	13,700	1.68	15,300	1.48	23,600	1.76
20,800	1.55	13,600	1.22	24,000	2.68	11,500	0.92	26,150	2.67	13,700	1.55	16,700	1.85	24,300	1.69
17,500	1.62	15,400	1.44	24,800	2.31	11,500	1.13	24,100	2.78	12,150	1.58	15,700	1.57	24,800	1.89
16,900	1.65	15,300	2.02	22,700	2.18	11,500	1.07	25,500	2.90	11,500	1.66	15,100	1.72	21,900	1.89
14,800	1.31	17,000	1.19	24,900	2.56	11,500	1.05	30,000	3.07	12,100	1.77	14,600	1.62	25,300	2.06
16,500	1.46	14,600	1.11	24,000	1.98	10,600	0.84	24,300	2.45	12,400	1.81	15,000	1.72	23,100	2.04
16,000	2.00	19,600	1.30	23,300	2.21	10,600	1.19	24,900	2.36	11,500	1.95	14,500	1.53	24,700	2.20
16,400	1.62	25,100	1.95	23,200	2.12	11,100	1.07	26,000	1.88	10,200	1.57	16,100	1.67	28,200	2.23
17,000	1.40	23,000	1.69	23,100	2.17	11,400	1.12	25,500	2.97	11,700	1.78	15,800	1.65	25,800	2.04
20,500	1.60	26,200	1.82	27,100	2.72	13,200	1.13	22,700	2.39	10,700	1.75	16,400	1.75	25,300	1.89
21,300	1.60	25,000	1.83	28,500	2.77	14,800	0.95	20,000	1.74	12,400	1.96	15,400	1.66	26,400	2.07
18,600	1.60	18,600	1.49	24,300	2.35	12,000	1.08	24,800	2.51	12,100	1.77	15,400	1.65	24,900	1.96

STATISTICAL ANALYSIS OF ASBESTOS LAMINATE DATA

An analysis of the test data was carried out using a random, pairwise sorting scheme whereby the means of each set of data generated from flexure tests (12 per laminate) were compared at the 95% probability level of the student t distribution. This scheme is summarized below.

1. The difference between any two observed sample means, $\bar{x}_i - \bar{x}_j$, and the standard error of the difference

$$\left[\frac{s_i^2 + s_j^2}{n} \right]^{1/2}$$

is computed.

2. These values are used to calculate the 95% confidence limits for the true population difference, $\mu_i - \mu_j$. Using the relation

$$\left(\bar{x}_i\right) - \left(\bar{x}_j\right) \pm t_{0.025} \left[\frac{s_i^2 + s_j^2}{n} \right]^{1/2}$$

3. If the lower confidence limit is greater than zero, the test result is that μ_i is greater than μ_j. If the upper confidence limit is less than zero, the opposite results; i.e., that μ_j is greater than μ_i. If the confidence limits result in too wide a spread, the decision is that no significant difference exists within the limits of sampling error, $\mu_i = \mu_j$.

The above is illustrated by the following graphic representation:

	< 0 (-)	> 0 (+)
Lower Limit $\left(\bar{x}_i\right) - \left(\bar{x}_j\right)$	$\mu_i = \mu_j$	$\mu_i > \mu_j$
Upper Limit $\left(\bar{x}_i\right) - \left(\bar{x}_j\right)$	$\mu_j > \mu_i$	$\mu_i = \mu_j$

Using the above simple pairwise statistical comparison of means, the eight sample means of both the room temperature ultimate flexural strength and modulus were sorted stepwise from the lowest to the statistically significant highest values as follows:

1. Compare $\overline{x}_i$ to $\overline{x}_j$ as above.

2. If $\overline{x}_i > \overline{x}_j$, exchange or permute the order of $\overline{x}_i$ and $\overline{x}_j$, and compare $\overline{x}_i$ to $\overline{x}_{j+1}$ as in Item 1.

3. If $\overline{x}_i < \overline{x}_j$, or $\overline{x}_i = \overline{x}_j$, do not exchange or permute the the order of $\overline{x}_i$ and $\overline{x}_j$ and compare $\overline{x}_j$ to $\overline{x}_{j+1}$ as in Item 1.

In this fashion, pairwise comparison will automatically move or "sweep" the highest statistically significant value(s), or $\overline{x}_i$, to the highest index value.

The results of this comparative sorting are tabulated for ease of reference in Table V. Laminates 1057, 1059, and 1062 were shown to be superior over all other laminates when flexural strength values were compared, but no significant difference could be ascertained between the three. When flexural moduli were compared, only Laminates 1057 and 1059 were superior, and there was no significant difference between the two. Laminate 1057 was eliminated from consideration because of the fragile character of the 5-mil asbestos paper, which made impregnation and processing difficult. Laminate 1062 was eliminated because the asbestos tended to rupture and extrude during lamination.

Laminate 1059, embodying Amercoat C10-G15 crocidolite asbestos mat, was selected as the best of the eight laminates processed. Influencing the decision was the overall superiority of the crocidolite asbestos fiber over the chrysotile fiber, including better tensile strength, less water of hydration, higher specific gravity, greater hardness, better chemical resistance, and more neutral pH (see Table VI and Figure 2). It was finally concluded that if Laminate 1059 could exhibit superior mechanical properties, even though it was one which exhibited the lowest physical properties (marginal specific gravity, high void content, low resin content, etc.), then it should continue to exhibit superior properties after optimization.

Some concern was expressed at this point for the rather marginal mechanical properties which were demonstrated. At the time, this was partly explained by nonoptimized processing conditions.

TABLE V

TABULATION OF STATISTICAL COMPARISON OF
ROOM TEMPERATURE FLEXURAL STRENGTH AND MODULUS

Laminate No.	i	Flexural Strength, X 10^{-3} psi		Comparison $(\bar{x}_i - \bar{x}_j)$	Std Error	$(\bar{x}_i - \bar{x}_j)$ Confidence Limits		Decision
		$\bar{x}_i$	$\bar{x}_j$			Lower	Upper	
				Flexural Strength				
1055	1	18.63	8.19					
				+ 0.02	1.61	- 3.32	+ 3.36	$\bar{x}_1 = \bar{x}_2$
1056	2	18.61	22.83					
				- 5.70	1.47	- 8.74	- 2.66	$\bar{x}_3 > \bar{x}_2$
1057	3	24.31	2.97					
				+12.30	0.63	+11.00	+13.60	$\bar{x}_3 > \bar{x}_4$
1058	4	12.01	1.80					
				- 0.50	0.88	- 2.32	+ 1.32	$\bar{x}_3 = \bar{x}_5$
1059	5	24.81	6.37					
				+12.73	0.78	+11.12	+14.34	$\bar{x}_5 > \bar{x}_6$
1060	6	12.08	1.03					
				+ 9.40	0.76	+ 7.83	+10.97	$\bar{x}_5 > \bar{x}_7$
1061	7	15.41	0.53					
				- 0.08	0.86	- 1.86	+ 1.70	$\bar{x}_5 = \bar{x}_8$
1062	8	24.89	2.40					
Decision Summary $\bar{x}_3 = \bar{x}_5 = \bar{x}_8 > \bar{x}_1$, $\bar{x}_2$, $\bar{x}_4$, $\bar{x}_6$ and $\bar{x}_7$.								
				Flexural Modulus				
1055	1	1.60	0.03					
				+ 0.12	0.108	- 0.10	+ 0.34	$\bar{x}_1 = \bar{x}_2$
1056	2	1.48	0.11					
				- 0.87	0.119	- 1.12	- 0.62	$\bar{x}_3 > \bar{x}_2$
1057	3	2.35	0.06					
				+ 1.27	0.076	+ 1.11	+ 1.43	$\bar{x}_3 > \bar{x}_4$
1058	4	1.08	0.01					
				- 0.19	0.135	- 0.47	+ 0.19	$\bar{x}_3 = \bar{x}_5$
1059	5	2.54	0.16					
				+ 0.77	0.126	+ 0.51	+ 1.03	$\bar{x}_5 > \bar{x}_6$
1060	6	1.77	0.03					
				+ 0.89	0.119	+ 0.69	+ 1.14	$\bar{x}_5 > \bar{x}_7$
1061	7	1.65	0.01					
				+ 0.58	0.261	+ 0.32	+ 0.84	$\bar{x}_5 > \bar{x}_8$
1062	8	1.96	0.03					
Decision Summary $\bar{x}_3 = \bar{x}_5 > \bar{x}_1$, $\bar{x}_2$, $\bar{x}_4$, $\bar{x}_6$, $\bar{x}_7$ and $\bar{x}_8$.								

TABLE VI

COMPARISON OF CROCIDOLITE AND
CHRYSOTILE ASBESTOS FIBERS*

Property	Chrysotile	Crocidolite
Max. Tensile Strength	824,000 psi	1,000,000 psi
Young's Modulus	23.2 x 10^6 psi	27.1 x 10^6 psi
Fiber Length	1/32-1/4 in.	1/8-3,0 in.
Fiber Diameter	0.03 μ	0.1 μ
Essential Composition	Hydrous silicate of magnesia	Silicate of sodium and iron with some water
Percentage Water	12.0%-15.0%	2.5%-4.5%
Hardness, Mohs	2.5-4.0	4.0
pH	9.2-9.8 Highly alkaline	6.02** Slightly acidic
Specific Gravity	2.4-2.6	3.2-3.3
Heat Resistance	Excellent	Excellent

* Sources: Handbook of Asbestos Textiles, second edition, Asbestos
  Textile Institute; A. A. Hodgson, "Fibrous Silicates," Lecture
  Series, Cape Asbestos Fibres Limites, 114 and 116 Part Street,
  London W-1, England; and Robert E. Cryor, "Asbestos Reinforced
  Plastics Resist Heat and Chemicals," Materials in Design Engi-
  neering (April 1966).

** Narmco determination.
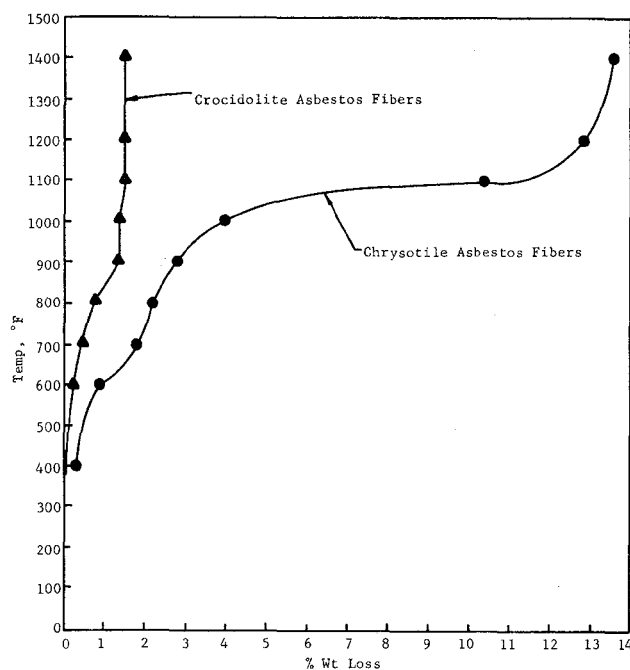
Source: Handbook of Asbestos Textiles, second edition, Asbestos
        Textile Institute.

Figure 2. Effect of Temperature on Weight
           Loss of Asbestos Fibers

LITERATURE REFERENCES STRESSING CAUTION IN SELECTION OF CROCIDOLITE FOR
HIGH-TEMPERATURE EXPOSURE

1. "Its resistance to heat is lower than that of chryosotile but its
    tensile strength is generally very high....." Handbook of Asbestos
    Textiles, 2nd edition, Asbestos Textile Institute, p. 6.

2. "At ordinary temperature, blue asbestos is considered stronger than
    chrysotile, but even at heating beyond the low temperature of 400°F,
    blue asbestos loses some of its strength, while chrysotile is not
    affected even at temperatures up to 700°F.

    It is reported that chrysotile has little decrease in strength in
    saturated steam and in moist air in temperatures up to 400°F.
    Above 400°F blue asbestos loses strength to a much greater extent
    in moist than in dry air. At this temperature it undergoes de-
    composition." Asbestos, Rosato, p. 51.

3. "Decrease in Strength of Asbestoses After Exposure to Heat for
    Constant Periods (3 min, 60 min) at Variable and Constant Tempera-
    ture, Table 18:

Type	°C	Strength, kp/mm^2	Decrease in Strength, %
Chrysotile	--*	42.0-52.0	24.0-35.8
Crocidolite	--*	99.0	64.2

    * Strengths @ 20°C after 60 minutes at
      375°±10°C.

    from Asbestos Fundamentals, Berger & Oesper, p. 94.

4. "In the case of crocidolite oxidation is also involved. The maximum
    loss of weight by crocidolite is reached near 650°C (higher tempera-
    tures result in a gain of weight)." Asbestos Fundamentals, Berger,
    p. 90.

5. "It is true that an oxidation occurs with crocidolite at 400°C
    (750°F), but if this is precluded by heating the fiber in an
    inert atmosphere, the change in tensile strength still takes
    place." Fibrous Silicates, A. A. Hodgson, p. 25.

6. "A significant exothermic reaction of crocidolite at 400°C (750°F)
    in oxidizing conditions, due to the oxidation of some of its ferrous
    iron to ferric iron.

7. "An oxidation process occurs at 400°C (750°F) and although dehydration
    curves point to the loss of water, curves for weight loss do not."
    Fibrous Silicates, A. A. Hodgson, p. 31.

SECTION III

LAMINATE PROCESS STUDIES

PROCEDURES INVESTIGATED

Laminate process studies based on the Amercoat C10-G15 crocidolite asbestos mat were initiated. Although crocidolite asbestos contains less water of hydration and is less susceptible to water damage than chrysotile, the mat was dried for 1/2 hour at 250°F prior to impregnation. Impregnation with Skybond 700 polyimide resin was carried out by drawing 9-in. wide strips of the 20-mil mat through a laboratory coater equipped with dip tank and spring-loaded doctor blades (see Figures 3 and 4). The resin was used without dilution (60%-64% solids). Saturation of the mat was evident from the translucent appearance. The impregnated strips of mat were subsequently B-staged in an air circulating oven regulated at 250°F. B-stage resin pickup and volatiles determinations were made. The foregoing procedures were identical to those employed during the asbestos reinforcement selection studies. The equivalent laminate, used as a control here, was designated 1059.

A chrysotile asbestos fibers processor cautioned us originally that the alkaline nature of these fibers could very possibly cause a chemical inter- action with the Skybond 700 polyimide resin, which is considerably acidic (pH 4.0-4.7). The pH of the crocidolite mat (see Table VI) was determined to be 6.02, or slightly acidic, and considerably more compatible with the polyimide than the chrysotile fiber.

The first laminate made was 1059A (see Table VII) as part of a reproduci- bility study. This was considered to be desirable as a quality control pro- cedure on the commercial asbestos mat, and as a check on the process. The latter is identical to the former process. The room temperature flexural strength was comparable with that of Laminate 1059, definitely indicating that reproducibility was possible. Remaining portions of Laminates 1059 and 1059A were cut into specimens, heat aged for 1 hour and 100 hours at 600°F in air, and subsequently tested in flexure. It was extremely encouraging to note that as much as 67.8% of the initial room temperature flexural strength was retained after 1 hour at 600°F when tested at 600°F, and as much as 74.3% of the initial room temperature flexural strength was retained after 100 hours at 600°F when tested at 600°F. Good thermal stability and oxidation resistance at 600°F appeared to be inherent in the system.

A press cure procedure employing barrier and breather materials (see Appendix I) on each side of the laminate has been used. This was essential for volatile release and management of excess resin. The barrier acted as a "molecular sieve" by restraining resin flow but passing volatiles which were in turn carried off by the breather fabric. A laminate made by being cured immediately against metal caul plates had a crazed and cracked surface from trapped volatiles, indicating the need for a breather for volatile release during lamination. The Monsanto postcure (up to 700°F in air) has been em- ployed without modification to date.
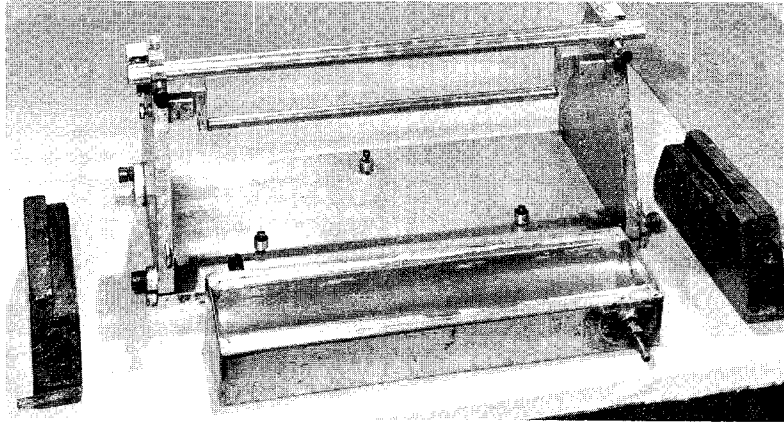
Figure 3.   Exploded View of Laboratory Dip
            Tank Coater

Figure 4.   Technician Impregnating
            Amercoat C10-G15 Crocido-
            lite Asbestos Mat with
            Skybond 700 Polyimide
            Resin Using Laboratory
            Dip Tank Coater

TABLE VII

THE EFFECT OF BINDER REMOVAL FROM ASBESTOS MAT ON LAMINATE PROPERTIES AND REPRODUCIBILITY STUDY

Laminate No. (Condition)	B-Stage & Panel Properties						
	% Pickup	% Volatile	% Flow	% Resin (calc.)	% Voids	Sp Gr	Mils/Ply
1059	67.7	20.2	55.2	27.68	27.4* (27.4)	1.70 (1.70)	9.0 (8.7)
1059A (Repeat)	66.5	24.8	52.7	28.9	19.9 (22.9)	1.85 (1.78)	9.4 (9.3)
1095 (Pyrolysis @ 1050°F)	71.6	28.0	57.8	32.7	14.0 (19.9)	1.91 (1.78)	8.5 (9.2)
1095A (Pyrolysis @500°F)	70.4	22.5	55.9	32.8	20.7 (23.0)	1.76 (1.71)	9.2 (9.2)

Laminate No. (Condition)	RT Flexure Properties		Flexure Properties at 600°F after 1 hr @ 600°F in Air		% Strength Retention	Initial Individual Specimen Properties					Flexure Properties @ 600°F after 100 hr @ 600°F in Air		% Strength Retention	% Wt Loss
	Strength, psi	Modulus, psix10⁻⁶	Strength, psi	Modulus, psix10⁻⁶		Specimen No.	% Resin	Vol % Void	Sp Gr	Mils/Ply	Strength, psi	Modulus, psix10⁻⁶		
1059	30,500	3.57	18,700	3.27	62.4	3	29.2	--**	--	8.0	17,300	2.93	58.5	2.99
	28,500	3.30	17,800	2.45		6				8.2	16,200	2.97		3.38
	24,500	3.71	15,800	2.89		9				8.4	14,800	2.71		3.53
	27,800	3.53	17,400	2.87							16,700	2.87		
1059A (Repeat)	23,100	2.74	14,900	2.15	67.8	3	30.0	24.8	1.82	8.5	17,600	3.09	74.3	4.40
	25,900	2.82	13,700	2.28		6	29.0	25.5	1.82	9.0	18,800	3.05		4.41
	20,000	2.80	17,800	2.49		9	28.5	26.3	1.81	8.6	17,900	3.25		4.28
	20,700	2.62	16,200	2.50		12	29.6	26.8	1.78	8.8	14,500	1.85		4.38
	23,100	2.74	15,700	2.35							17,200	2.81		
1095 (Pyrolysis @ 1050°F)	7,960	1.78	7,810	1.63	95.0	3	27.0	--**	--	8.3	6,790	1.64	84.5	3.10
	7,660	1.58	8,270	1.66		6				8.5	6,370	1.34		3.10
	9,550	2.03	7,680	1.57		9				8.5	8,090	2.00		2.86
	8,390	1.80	7,920	1.62							7,080	1.66		
1095A (Pyrolysis @ 500°F)	19,200	2.62	15,300	2.57	80.5	3	25.7	--**	--	9.5	14,900	2.51	82.2	2.89
	16,000	2.30	14,800	2.48		6	25.7			9.5	14,900	2.25		2.79
	18,800	2.54	12,400	1.73		9	28.8			9.2	13,800	2.19		2.60
	18,000	2.48	14,500	2.26							14,800	2.32		

* Before postcure. Parenthetical value signifies after postcure.

** Panel only

NOTE: Processing Information

Asbestos:	Amercoat C10-G15 crocidolite mat
Resin:	Skybond 700 polyimide
B-Staging:	25 min @ 250°F
Size:	9-in. x 9-in. x 10-ply laminates
Press Cure:	Two 2-ply TFE 30/116 barrier + 4 plies 1500 style glass fabric breather on each side; 30 min @ 500 psi; in hot, out cold
Postcure:	2 hr each @ 392°F, 437°F, 482°F, 572°F, 617°F, and 662°F, + 4 hr @ 700°F in air-circulating oven
Testing:	Per Narmco ETM 201; FTM 406, Metlbond 1031; ASTM D-790; and ATC Report ARTC-11, Method VIII

Table VII also shows the results of a study where the asbestos mat was prolyzed at 500°F and 1050°F before impregnation to remove the polyester binder (3%-7%). The effect of the polyester binder is not completely understood at present. Although not a good thermally stable resin, it does not apparently detract appreciably from the strength retention of this system at 600°F. More importantly, the effect of the binder on degree of impregnation with Skybond 700 polyimide resin is not known. Figure 5 shows weight loss on the mat in air at 500°F.
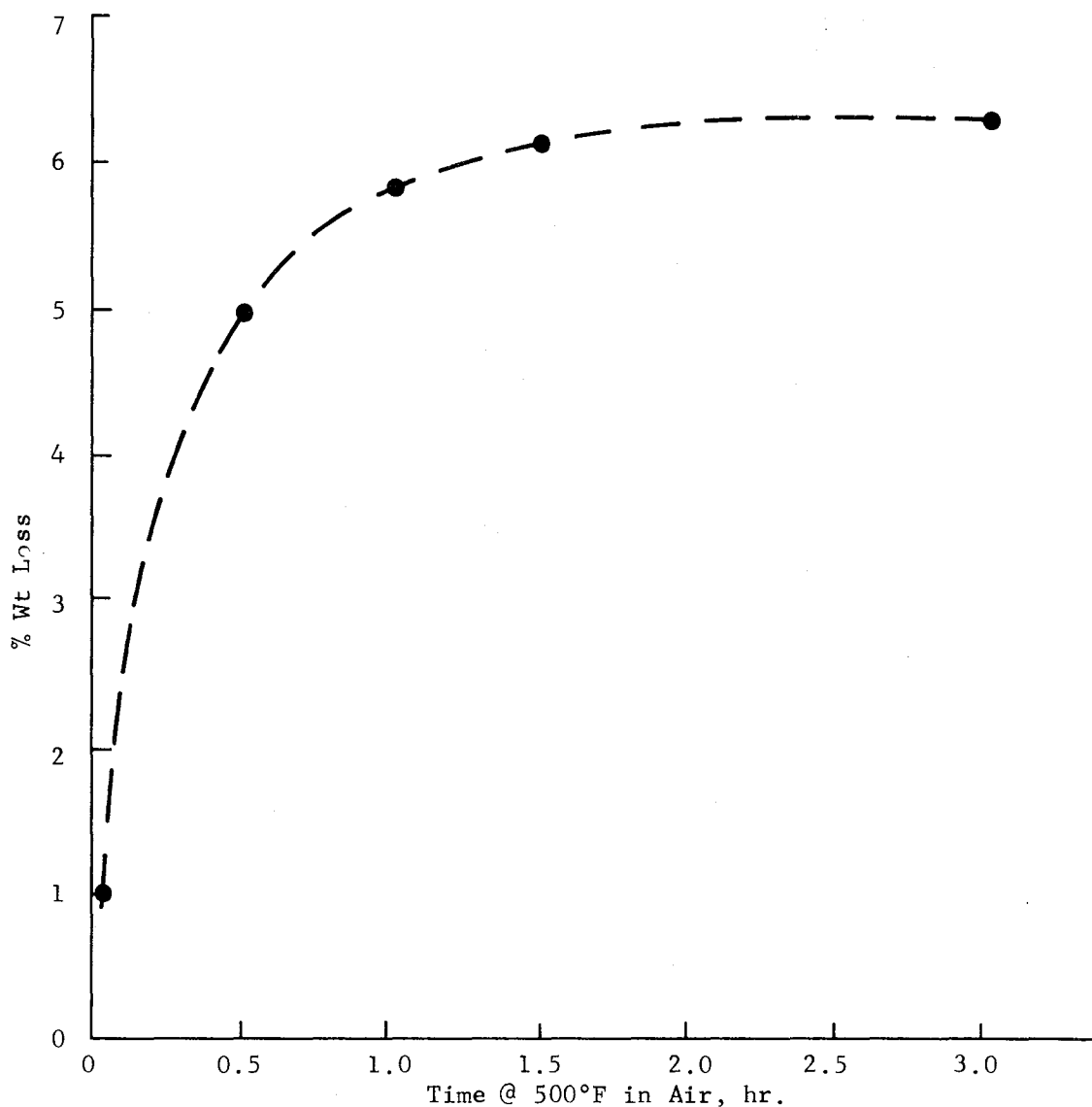
Figure 5.   Percent Weight Loss of Amercoat C10-G15
Crocidolite Asbestos Mat at 500°F in
Air As Related to Polyester Binder

19

The next process variable studied was rate of heat rise from room temperature to 350°F prior to application of laminating pressure. Table VIII includes results for Laminates 1100 and 1100B. The prepreg held at 15 and 25 minutes at 250°F was too far advanced to undergo a rapid heat rise of 10°F/minute prior to application of pressure. Unsuccessful lamination resulted.

Rate of heat rise was next studied from the standpoint of applying laminating pressure at room temperature, followed by raising the temperature to 350°F at rates from 2°F to 10°F/minute. Results are also shown in Table VIII. The laminate physical properties (e.g., specific gravity, resin content, mils/ply) and mechanical properties (e.g., flexural strength) did not respond to these variations, and a trend was not apparent. The room temperature flexural strength was constant, for all practical purposes, at roughly 20,000 psi.

The next process variable studied was laminating pressure: 100 to 1000 psi. Table IX lists Laminates 1096 through 1099 and the results of this study. The laminate physical properties responded very well to these variables; however, the mechanical properties were once again affected very little.

The next process variables studied were B-stage time at 250°F and laminating temperature (see Table X). It was believed that this set of experiments would cause a laminate response which would rapidly indicate the shortest path to the best process.

The study of these variables was expected to offer an excellent profile of prepreg pickup and volatiles and laminate flow, resin content, specific gravity, and mils per ply thickness, with attendant good response in laminate mechanical properties. The anticipated profile expected was attained for laminate physical properties. Once again, however, the anticipated response in laminate flexural strength was not observed, as indicated by the partial data that were obtained.

LAMINATE NO. 1097 (See Table X)

| Individual Specimen Properties | | | | | | Laminate Properties* | | | |
Speci-men No.	% Resin	Vol % Void	Sp Gr	Mils/ Ply		Strength, psi	Modulus, psi x 10⁶	% Strength Retention	% Wt Loss
3	28.4	21.9	1.67	9.5		13,500	2.01	70.5	3.04
6	26.8	22.9	1.68	9.9		14,500	2.26		2.83
9	29.0	18.9	1.63	9.8		14,800	2.24		3.30
12	27.1	22.8	1.68	9.6		13,800	2.20		3.16
						14,100	2.18		

Further process studies, per se, and completion and analysis of data were abandoned in favor of finding the reason for the lack of response to broad process variations in laminate mechanical properties.

OPERTIES

Initial Individual Specimen Properties					Flexure Properties @ 600°F after 100 hr @ 600°F in Air		% Strength Reten- tion	% Wt Loss
Speci- men No.	% Resin	Vol % Void	Sp Gr	Mils/ Ply	Strength, psi	Modulus, $psi \times 10^{-6}$		
3	39.1	14.1	1.58	11.7	11,100	1.60	64.4	4,35
6	38.5	14.9	1.59	11.3	12,700	1.74		4.11
9	37.4	17.2	1.62	11.5	12,300	1.65		4.13
12	36.6	15.1	1.59	11.3	11,500	1.77		3.99
					11,900	1.69		
3	28.4	21.9	1.67	9.5	13,500	2.01	70.5	3.04
6	26.8	22.9	1.68	9.9	14,500	2.26		2.83
9	29.0	18.9	1.63	9.8	14,800	2.24		3.30
12	27.1	22.8	1.68	9.6	13,800	2.20		3.16
					14,100	2.18		
3	30.0	24.8	1.82	8.5	17,600	3.09	74.3	4.40
6	29.0	25.5	1.82	9.0	18,800	3.05		4.41
9	28.5	26.3	1.81	8.6	17,900	3.25		4.28
12	29.6	26.8	1.78	8.8	14,500	1.85		4.38
					17,200	2.81		
3	25.8	26.7	1.73	9.9	12,400	2.18	67.4	3.30
6	25.9	25.2	1.71	9.9	12,500	2.11		3.66
9	25.6	27.4	1.74	9.5	13,000	2.13		3.37
12	22.3	32.3	1.80	9.7	15,100	2.49		2.95
					13,200	2.22		
3	21.9	33.1	1.81	8.1	15,700	2.20	62.0	2.90
6	21.5	34.6	1.83	8.5	14,600	2.39		3.08
9	20.6	34.7	1.83	8.5	14,900	2.16		3.26
12	20.1	36.2	1.85	8.6	15,500	2.56		3.03
					15,200	2.33		

TABLE IX

THE EFFECT OF LAMINATING PRESSURE ON LAMINATE PR

| Laminate No. (Condition) | B-Stage & Panel Properties | | | | | | | RT Flexure Properties | | Flexure Properties at 600°F after 1 hr @ 600°F in Air | | % Strength Retention | S |
	% Pickup	% Volatile	% Flow	% Resin (calc.)	Vol % Void	Sp Gr	Mils/ Ply	Strength, psi	Modulus, psix10^{-6}	Strength, psi	Modulus, psix10^{-6}		
1096 (100 psi)	68.0	26.3	49.9	36.1	25.2* (26.1)	1.61 (1.59)	12.2 (11.2)	20,000 15,200 22,600 <u>16,700</u> 18,500	2.19 2.22 2.38 <u>1.88</u> 2.17	14,000 12,200 14,200 <u>13,000</u> 13,400	1.75 1.64 1.98 <u>1.63</u> 1.75	72.3	1
1097 (300 psi)	70.1	24.5	58.9	27.3	26.9 (29.9)	1.72 (1.65)	10.0 (0.2)	17,700 22,200 18,200 <u>21,800</u> 20,000	1.83 2.32 2.31 <u>2.39</u> 2.21	15,600 15,800 15,400 <u>15,700</u> 15,600	2.00 2.29 2.27 <u>2.44</u> 2.25	77.9	1
1059A (500 psi)	66.5	24.8	52.7	28.9	20.0 (23.0)	1.85 (1.78)	9.4 (9.3)	25,900 25,900 20,000 <u>20,700</u> 23,100	2.73 2.82 2.80 <u>2.62</u> 2.74	14,900 13,700 17,800 <u>16,200</u> 15,700	2.15 2.28 2.49 <u>2.50</u> 2.35	67.8	1
1098 (750 psi)	67.0	20.7	55.1	26.2	21.8 (26.0)	1.86 (1.76)	9.2 (9.2)	18,100 19,400 18,700 <u>22,000</u> 19,600	2.16 2.55 2.22 <u>2.11</u> 2.26	16,300 12,700 13,800 <u>13,200</u> 14,000	2.36 2.01 2.32 <u>2.19</u> 2.22	71.4	
1099 (1000 psi)	66.6	23.6	55.6	24.7	19.0 (24.0)	1.96 (1.84)	8.7 (8.7)	25,100 24,800 24,900 <u>23,300</u> 24,500	2.71 2.55 2.39 <u>2.44</u> 2.52	17,600 15,700 16,100 <u>13,400</u> 15,700	2.89 2.45 2.33 <u>2.47</u> 2.54	64.0	

* Before postcure. Parenthetical value signifies after postcure.

** In test.

NOTE: <u>Processing Information</u>

Asbestos: Amercoat C10-G15 crocidolite mat

Resin: Skybond 700 polyimide

B-Staging: Time @ 250°F as indicated

Size: 9-in. x 9-in. x 10-ply laminates

Press Cure: Two 2-ply TFE 30/116 barrier + 4 plies 1500 style glass fabric breather on each side; 30 min @ indicated temp @ 300 psi; in hot, out cold

Postcure: 2 hr each @ 392°F, 437°F, 482°F, 572°F, 617°F, & 662°F, + 4 hr @ 700°F in air-circulating oven

Testing: Per Narmco ETM 201; FTM 406, Metlbond 1031; ASTM D-790; & ATC Report ARTC-11, Method VIII

TABLE X

EFFECT OF B-STAGING TIME AT 250°F
AND CURING TEMPERATURES ON LAMINATE PROPERTIES

Laminate No. (Condition)	B-Stage & Panel Properties							RT Flexure Properties		Flexure Properties at 600°F after 1 hr @ 600°F in Air		% Strength Retention
	% Pickup	% Volatile	% Flow	% Resin (calc.)	% Void	Sp Gr	Mils/ Ply	Strength, psi	Modulus, psiX10^{-6}	Strength, psi	Modulus psiX10^{-6}	
1097 (Control; 25 min; 350°F)	70.1	24.5	58.9	27.3	26.8* (29.7)	1.72 (1.65)	10.0 (9.2)	17,700 22,200 18,200 21,800 20,000	1.83 2.32 2.31 2.39 2.21	15,600 15,800 15,300 15,700 15,600	2.00 2.29 2.27 2.44 2.25	77.9
1107 (35 min; 450°F)	61.8	19.8	39.9	36.4	17.4 (20.2)	1.77 (1.71)	11.4 (11.2)	19,500 20,700 21,600 19,100 20,200	2.47 2.39 2.15 1.95 2.24	13,700 15,400 15,000 14,200 14,600	2.09 1.87 2.09 2.00 2.01	72.2
1108 (35 min; 550°F)	61.5	19.8	37.8	38.0	23.7 (25.1)	1.61 (1.58)	13.0 (13.0)	19,700 22,700 15,400 22,200 20,000	2.45 2.43 1.72 2.01 2.15	11,700 15,500 11,100 12,600 12,800	1.63 1.86 1.92 1.45 1.72	63.9
1109 (45 min; 450°F)	62.7	18.9	30.4	30.4	24.4 (26.6)	1.72 (1.67)	10.4 (10.6)	17,300 21,000 24,700 21,700 21,200	2.54 2.23 2.21 2.38 2.34	14,300 15,000 14,300 14,200 14,500	2.30 1.99 1.78 1.89 1.99	68.4
1110 (45 min; 550°F)	63.1	18.9	47.0	30.4	25.7 (27.4)	1.69 (1.65)	10.7 (11.0)	17,700 21,800 20,000 26,000 21,400	2.40 2.38 2.18 2.55 2.38	11,800 13,800 14,300 16,000 14,000	1.78 1.91 1.95 1.89 1.88	65.4
1111 (35 min; 350°F)	62.2	18.5	38.0	39.0	14.4 (20.1)	1.79 (1.67)	12.0 (10.9)	13,800 16,900 20,100 17,400 17,000	2.20 2.14 2.59 2.39 2.33	12,900 14,400 13,400 14,600 13,800	2.44 2.19 2.08 2.12 2.20	81.2
1112 (25 min; 450°F)	64.5	18.8	46.0	34.2	20.5 (17.3)	1.74 (1.81)	11.3 (10.5)	19,700 16,700 18,600 19,800 18,700	2.65 2.12 2.55 2.39 2.43	13,800 11,700 13,800 13,300 13,100	2.16 1.91 1.90 1.99 1.99	70.0
1113 (45 min; 350°F)	63.3	11.6	33.7	44.6	12.4 (12.4)	1.74 (1.74)	13.7 (12.3)	22,400 20,000 19,900 21,900 21,100	2.25 1.99 1.88 1.95 2.02	15,000 14,700 14,200 14,300 14,600	1.78 1.76 1.72 1.94 1.80	69.2
1115 (55 min; 350°F)	59.0	18.1	24.9	44.8	14.3 (--)	1.70 (--)	13.3 (--)	--**	--**	--**	--**	--**

* Before postcure. Parenthetical value signifies after postcure.

** Data will not be completed.

NOTE: Processing Information

Asbestos:	Amercoat C10-G15 crocidolite mat	Size:	9-in. × 9-in. × 10-ply laminates
Resin:	Skybond 700 polyimide	Press Cure:	Two 2-ply TFE 30/116 barrier + 4 plies 1500 style glass fabric breather on each side; 30 min @ indicated temp @ 300 psi; in hot, out cold
B-Staging:	Time @ 250°F as indicated		
		Postcure:	2 hr each @ 392°F, 437°F, 482°F, 572°F, 617°F, & 662°F, + 4 hr @ 700°F in air-circulating oven

RELATIONSHIP BETWEEN REINFORCEMENT AND RESIN PARAMETERS AND MARGINAL
COMPOSITE MECHANICAL PROPERTIES

1.   It was apparent at this point that a very serious problem was preventing
process optimization and attendant upgrading of laminate mechanical properties.
An intensive effort was undertaken to uncover the problem and effect its solu-
tion.   Existing data were first analyzed prior to proceeding with exploratory
process parameters.

   A very pronounced linear relationship was noted to exist between laminate
resin content and laminate void content (see Appendix II).   Figure 6 illustrates
the existing relationship for all laminates thus far processed.   Extrapolating
the line to zero void content, it might be concluded that resin content may be
roughly 60%.   Void content and resin content alone at this point could not
explain the marginal mechanical properties.
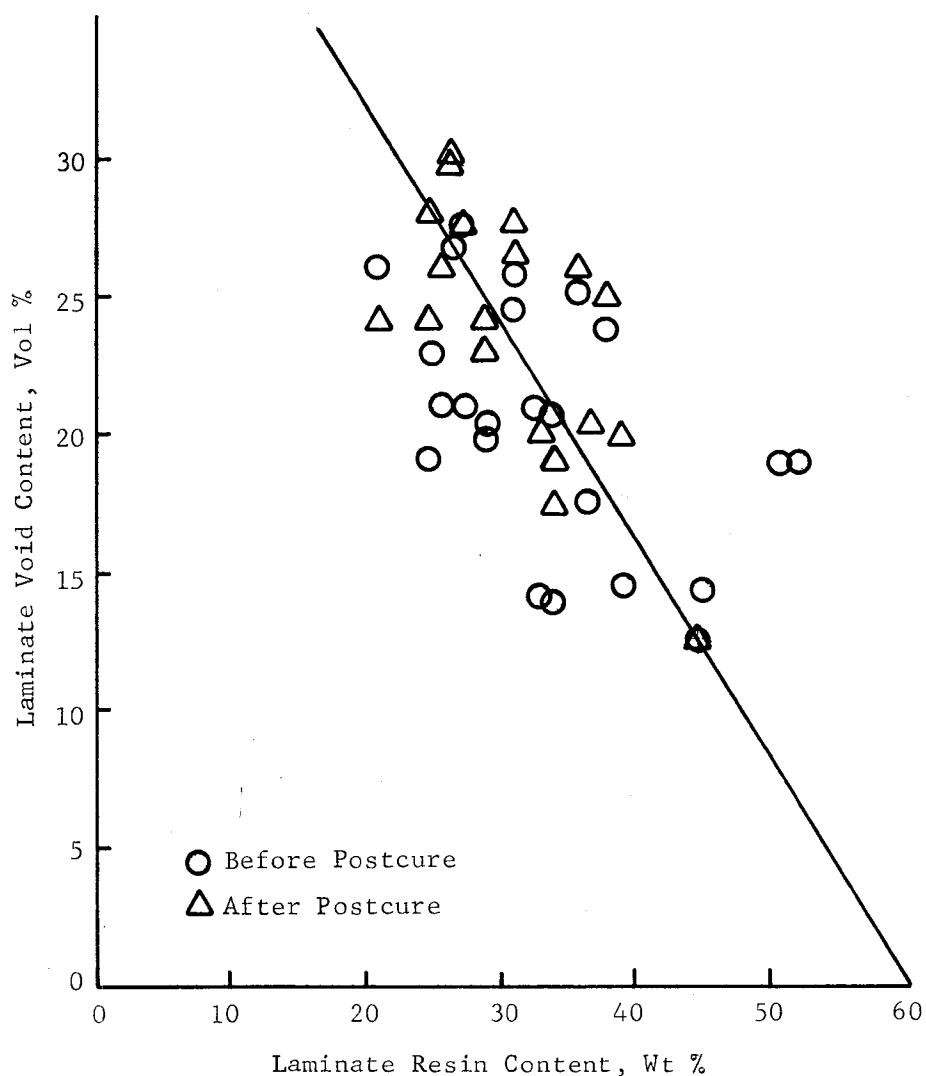
Figure 6.   Relationship Between Resin Content and Void
            Content for All Laminates Thus Far Processed

2. Another observation drawn from existing data was that all laminates were losing strength somewhere between 3.5% and 18.9% weight loss during the standard postcure up to 2 hours at 700°F in air (see Table XI). The loss tended to decrease when B-staging time and/or temperature was increased, or when curing temperature was raised from 350°F to 550°F. The loss tended to increase when the same variables were decreased or lowered. In any case, the average flexural strength loss at all levels was essentially the same and did not indicate any trend. It was postulated that the trapped volatile loss on postcure would have to be less than 3.5% before mechanical strength could be upgraded.

TABLE XI

WEIGHT LOSS OF SKYBOND 700 LAMINATES AFTER
STANDARD 700°F POSTCURE DUE TO TRAPPED VOLATILES
AND CORRELATION WITH ULTIMATE FLEXURAL STRENGTH

Laminate No.	B-Stage Conditions	Cure Conditions	% Wt Loss on Postcure	Avg Ult Flexural Strength, psi
1055	25 min, 250°F	30 min, 350°F, 500 psi	--	18,600
1056			12.1	18,600
1057			14.4	24,300
1058			15.2	12,000
1059			9.8	24,800
1060			18.9	12,100
1061			13.3	15,400
1062			12.5	24,900
1059A			--	23,100
1095*			10.5	8,390
1095**			8.6	18,000
1096		30 min, 350°F, 100 psi	12.6	18,500
1097		30 min, 350°F, 300 psi	11.3	20,000
1098		30 min, 350°F, 750 psi	9.4	19,600
1099		30 min, 350°F, 1000 psi	10.1	24,500
1100A		2°F/min; 30 min, 350°F, 500 psi	--	15,300
1100B	15 min, 250°F	2°F/min; 30 min, 350°F, 500 psi	--	17,259
1101	25 min, 250°F	2°F/min; 30 min, 350°F, 500 psi	13.0	21,900
1102		4°F/min; 30 min, 350°F, 500 psi	11.9	18,900
1103		6°F/min; 30 min, 350°F, 500 psi	12.1	20,500
1104		8°F/min; 30 min, 350°F, 500 psi	11.6	20,900
1105		10°F/min; 30 min, 350°F, 500 psi	11.6	22,400
1107	35 min, 250°F	30 min, 450°F, 300 psi	7.7	20,200
1108	35 min, 250°F	30 min, 550°F, 300 psi	4.5	20,000
1109	45 min, 250°F	30 min, 450°F, 300 psi	6.6	21,200
1110	45 min, 250°F	30 min, 550°F, 300 psi	3.5	21,400
1111	35 min, 250°F	30 min, 350°F, 300 psi	12.4	17,000
1112	25 min, 250°F	30 min, 450°F, 300 psi	7.5	18,700
1113	45 min, 250°F	30 min, 350°F, 300 psi	15.6	21,100
1115	55 min, 250°F	30 min, 350°F, 300 psi	16.9	20,400
1115A	55 min, 250°F	30 min, 350°F, 750 psi	13.9	16,500
1119***	25 min, 250°F	30 min, 350°F, 500 psi	11.9	20,700
1122***	25 min, 250°F	30 min, 350°F, 500 psi	--	--

   * Asbestos mat pyrolyzed at 1000°F to remove polyester binder.

  ** Asbestos mat pyrolyzed at 500°F to remove polyester binder.

*** Vacuum impregnated for good fiber saturation.

3. Consideration was immediately directed toward the quality of the batches of Skybond 700 polyimide resin and Amercoat C10-G15 crocidolite asbestos mat being used. A Skybond 700 laminate reinforced with 1581 style S-glass with HTS finish was made as a quality assurance procedure for the resin. The room temperature flexural strength after standard processing was close to data reported by Monsanto (see Table XII). It was concluded that the resin being used was of acceptable quality. The asbestos mat reinforcement was checked for quality by making an Epon 815 and Curing Agent Z laminate in which good fiber saturation and impregnation were attained. The flexural strength (see Table XII was again close to that reported for an epoxy system. Similarly, it was concluded that the quality of the crocidolite asbestos mat was also acceptable. We were in close contact with Monsanto, Amercoat Corporation, North American Asbestos Corporation, and Cape Insulation Ltd. (England) to confirm the foregoing.

TABLE XII

COMPARISON OF POLYIMIDE RESIN AND ASBESTOS REINFORCEMENT
WITH REPORTED DATA AS A QUALITY ASSURANCE PROCEDURE

	Reinforcement or Resin System	Resin Content, %	Sp Gr	RT Ult Flexural Strength, psi
Skybond 700 Laminates Reinforced with Glass Fabric				
1106	1581 Style S-glass (HTS) reinforcement	31.2	1.66	76,400
Reported Data*	181 Style E-glass (A-1100 Soft reinforcement)	Unknown	Unknown	75,000-85,000
Epoxy Laminates Reinforced with Amercoat C10-G15 Crocidolite Asbestos Mat				
1121-1	Epon 815, 20-phr Z curing agent resin system	--	1.71	37,900
1121-2		60.5	1.50	26,100
Reported Data 1**	Epoxy resin system	Unknown	1.6	42,000-43,000
Reported Data 2***		75	1.3	21,000

* Monsanto.

** R. E. Cryor, "Asbestos Reinforced Plastics Resist Heat and Chemicals," Materials in Design Engineering, April 1966.

*** V. E. Barrable et al., "Use of Crocidolite Asbestos in Reinforced Plastics," I&EC Product Research & Development, September 1963.

4. Suspecting that the trapped volatile evidenced in our laminates was a contributing factor to marginal strength, DuPont 8122 100% solids powdered polyimide resin was employed for studying a solvent-free system. The powder was sprinkled between dry plies of crocidolite mat, and the assembly was then placed in a press and laminated for 1 hour at 500°F at 1000 psi. The laminate developed an ultimate flexural strength of 40,200-42,300 psi, as shown in Table XIII. Compared with Skybond 700 laminates, it appeared that hot melt processing and a solvent-free system were advantageous.

TABLE XIII

COMPARISON OF CROCIDOLITE MAT REINFORCED LAMINATES MADE BY
HOT MELT AND SOLUTION IMPREGNATION WITH POLYIMIDE RESIN

Polyimide & Impregnation Technique	Process Conditions	Resin Content, %	Sp Gr	Void, %	RT Ult Flexural Strength, psi
DuPont 8122 Hot Melt	1 hr @ 500°F @ 1000 psi	25.4	1.95	22.85	40,200-42,300
Monsanto Skybond 700 Solution (N-methyl pyrrolidone)	Up to 30 min @ 550°F @ 1000 psi, plus 2-hr staged post-cure to 700°F	27-52	1.51-1.96	2.8-39.3	15,300-24,800

In furtherance of this solvent-free approach, a quantity of Skybond 701 was secured. This material is similar to Skybond 700, but has a slightly lower molecular weight and contains only ethanol (boiling point 170°F) as solvent, which can be more readily dried. Laminates were made with this material (see Table XIV). Although the volatiles remained high (13%-18%) in the prepreg, loss on postcure was reduced to 2.6% showing very few were trapped during cure. This gave rise to the suspicion that the greater portion of volatiles may be due to amide or imide formation during polymerization and not to solvent volatiles. The flexural strength was not improved by this technique.

5. Some consideration was next given to the flexure specimen configuration. First, a print-off or mark-off of the 116 style barrier fabric occurs in both flat surfaces. This can contribute to 2.5 mils per side or a total 5-mil error in specimen thickness when determining the cross section during flexure testing. Such an error could place the ultimate stress approximately 5000 psi below its actual level. Secondly, this same print-off could result in notching, which would cause localized or premature specimen failure, particularly in the tension side of the flexure specimen. Thirdly, we were pressing and testing the flexural specimens with random fiber orientation in the spanwise or direction X and Y planes and loading in the Z plane. It was decided to bond four 1/8-in. thick laminates together, taking the flexure specimen in a manner that

TABLE XIV

LAMINATES MADE WITH ALCOHOL-SOLUBLE SKYBOND 701
TO OVERCOME TRAPPED SOLVENT EFFECT

| Laminate No. | Processing | Panel Properties | | | | | | | % Wt Loss in Postcure | RT Flexural Strength, psi | RT Modulus, psi x 10^6 |
		% Pickup	% Volatile	% Flow	% Calc. Resin	% Void*	Sp Gr*	Mils/Ply*			
1123	B-staged 10 min @ 250°F; cured 30 min @ 600°F under 500-psi pressure	62.7	13.5	46.3	39.0	24.06 (25.8)	1.70 (1.66)	13.0 (13.2)	2.60	19,900 19,400 20,400 19,200 19,700	2.38 2.47 2.70 2.52 2.52
1124	B-staged 20 min @ 200°F; cured 30 min @ 350°F under 500-psi pressure	66.1	18.2	53.9	26.5	27.2 (30.0)	1.82 (1.75)	10.4 (10.0)	6.42	24,000 20,000 22,400 20,500 21,700	2.69 2.59 2.80 2.60 2.67

* Before postcure. Parenthetical number designates after postcure.

NOTE: Processing Information

Asbestos:	Amercoat C10-G15 crocidolite mat
Resin:	Skybond 700 polyimide
B-Staging:	25 min @ 250°F
Size:	9-in. x 9-in. x 10-ply laminates
Press Cure:	Two 2-ply TFE 30/116 barrier + 4 plies 1500 style glass fabric breather on each side; 30 min @ 350°F; in hot, out cold
Postcure:	2 hr each @ 392°F, 437°F, 482°F, 572°F, 617°F, & 662°F, + 4 hr @ 700°F in air-circulating oven

would allow flexural loading 90° from the above test, or in the X plane with random fiber orientation in the Y and Z planes. The result was a flexural ultimate strength of 21,700 psi in the former condition and 23,500 psi in the latter condition. It was concluded at this state that fiber orientation had little effect on flexural strength, especially because the composite flexural strength was very close to the shear strength expected for the resin.

6.   It was decided that some far-reaching processing variables would have to be investigated on a screening basis in order to find what actually caused this strength problem before a solution could be effected. Small (10-ply $\times$ 4.5-in. $\times$ 4.5-in.) laminates were prepared, varying processing conditions as deemed advisable and determining flexural strength on a screening basis. Table XV is a tabulation of this effort, outlining the processing variables and flexural strength where the laminate was considered worthy of testing.

Photomicrographs were made of polished sections from failed flexure specimens. Magnifications up to 1500X, the capability of optical equipment, were not sufficient to ascertain the degree of fiber wetting and impregnation and general nature of the matrix.

A sample of Skybond 700 was vacuum-dried 16 hours at 150°F at 30 in. Hg to a dry, friable powder. The resultant powder gelled almost immediately when sprinkled on a surface heated to 600°F. Flow at 350°F was very short before gelation. The weight loss of this material due to water in imide formation was 22.9% by weight after 10 minutes at 450°F. By direct comparison, the DuPont 8122 polyimide lost 15.5% under identical conditions. Weight loss alone could not be expected to be the reason for poor strength from the Skybond 700 polyimide.

A noticable improvement appeared to occur when dry plies of asbestos mat were interleaved with standard asbestos mat prepregged with Skybond 700. Table XV and Laminates 9, 10, 15, 17, and 21 gave average flexural strengths as high as 32,600 psi, depending on processing conditions. The dry ply apparently gives the volatiles a place to go or escape and possibly enhances the hydraulic action and resin management, even though dry ply tends to defeat the purpose of good fiber wetting and impregnation.

7.   Typical specific gravity and weight percent resin data taken from foregoing polyimide asbestos laminates were plotted on a specific gravity versus weight and volume percent resin chart (see Figure 7). It was interesting to note once again that the points fell in a cluster at a substantial distance from the theoretical weight percent resin curve. The departure from this theoretical line is a direct measure of percentage voids in the composite. We knew there was a large percentage of voids (averaging 25.5% by volume), resulting from poor wetting of asbestos and an outgassing resin matrix, but it now appeared that the asbestos fibers are especially senssitive to void content and may be incapable of optimum reinforcement unless void content is very low and plotted properties fall close to the theoretical curve described.

TABLE XV

SCREENING OF PROCESS VARIABLES FOR SKYBOND 700 AND
CROCIDOLITE ASBESTOS LAMINATES TO UPGRADE MECHANICAL STRENGTH

(4.5-in. x 4.5-in. x 10-ply Laminates)

| Laminate No.	Process Variables	RT Flexural Strength, psi
1	Press B-stage 55 min @ 250°F; contact @ 350°F; 30 min @ 350°F @ 300 psi	--
2	Three resin dips with air dry; B-stage 55 min @ 250°F; 30 min @ 350°F @ 300 psi	--
3	B-stage 75 min @ 250°F; 1.5-2.5 min contact @ 600°F; 30 min @ 600°F @ 750 psi; postcured	19,100
4	B-stage 75 min @ 250°F; 1.5-2.5 min contact @ 600°F; 30 min @ 600°F @ 1000 psi	--
5	Resin diluted with isopropanol; B-stage 75 min @ 250°F; 1.5-2.5 min contact @ 600°F; 30 min @ 600°F @ 750 psi	--
6	Resin diluted with isopropanol; B-stage 75 min @ 250°F; no barrier or breather; 30 min @ 350°F @ 2000 psi	--
7	B-stage 75 min @ 250°F; 30 min @ 350°F @ 3000 psi	--
8	B-stage 75 min @ 250°F; 30 min @ 350°F @ 3000 psi	--
9	Dry/wet ply 3/8; 30 min @ 350°F @ 500 psi	24,900
10	Dry/wet ply 5/6; 30 min @ 600°F @ 500 psi (28.8% calculated resin)	32,600
11	Prepreg cured; recoated, B-staged, & relaminated @ 350°F	--
12	Asbestos mat treated with 20% hydrochloric acid; B-staged 25 min @ 250°F; 30 min @ 350°F @ 500 psi; postcured	20,300
13	Asbestos mat treated with 20% sodium hydroxide; B-staged 25 min @ 250°F; compression molded 30 min @ 600°F @ 1000 psi	15,000
14	Asbestos mat without polyester binder; B-staged 25 min @ 250°F; compression molded 30 min @ 600°F @ 1000 psi	--
15	Dry/wet ply 6/3; B-staged 25 min @ 250°F; 30 min @ 600°F @ 500 psi (30% calculated resin)	20,000
16	High resin pickup; B-staged 25 min @ 250°F; 30 min @ 600°F @ 500 psi (31.8% calculated resin)	22,000
17	Dry/wet ply 6/4; B-staged 25 min @ 250°F; 30 min @ 600°F @ 500 psi (21.1% calculated resin)	32,900
18	Medium resin pickup; B-staged 25 min @ 250°F; 30 min @ 600°F @ 500 psi (24.8% calculated resin)	--
19	Low resin pickup; B-staged 25 min @ 250°F; 30 min @ 600°F @ 500 psi	--
20	Vacuum dry prepreg; 16 hr @ 150°F; 30 min @ 600°F @ 500 psi	29,700
21	Vacuum dry prepreg; 16 hr @ 150°F; dry/wet 3/2; 30 min @ 600°F @ 500 psi	27,700
22	1-ply Laminate; B-staged 25 min @ 250°F; 30 min @ 600°F @ 500 psi (21.8% calculated resin); 18.0 mils/ply	26,500
23	1-ply Laminate; B-staged 25 min @ 250°F; 30 min @ 350°F @ 500 psi	--
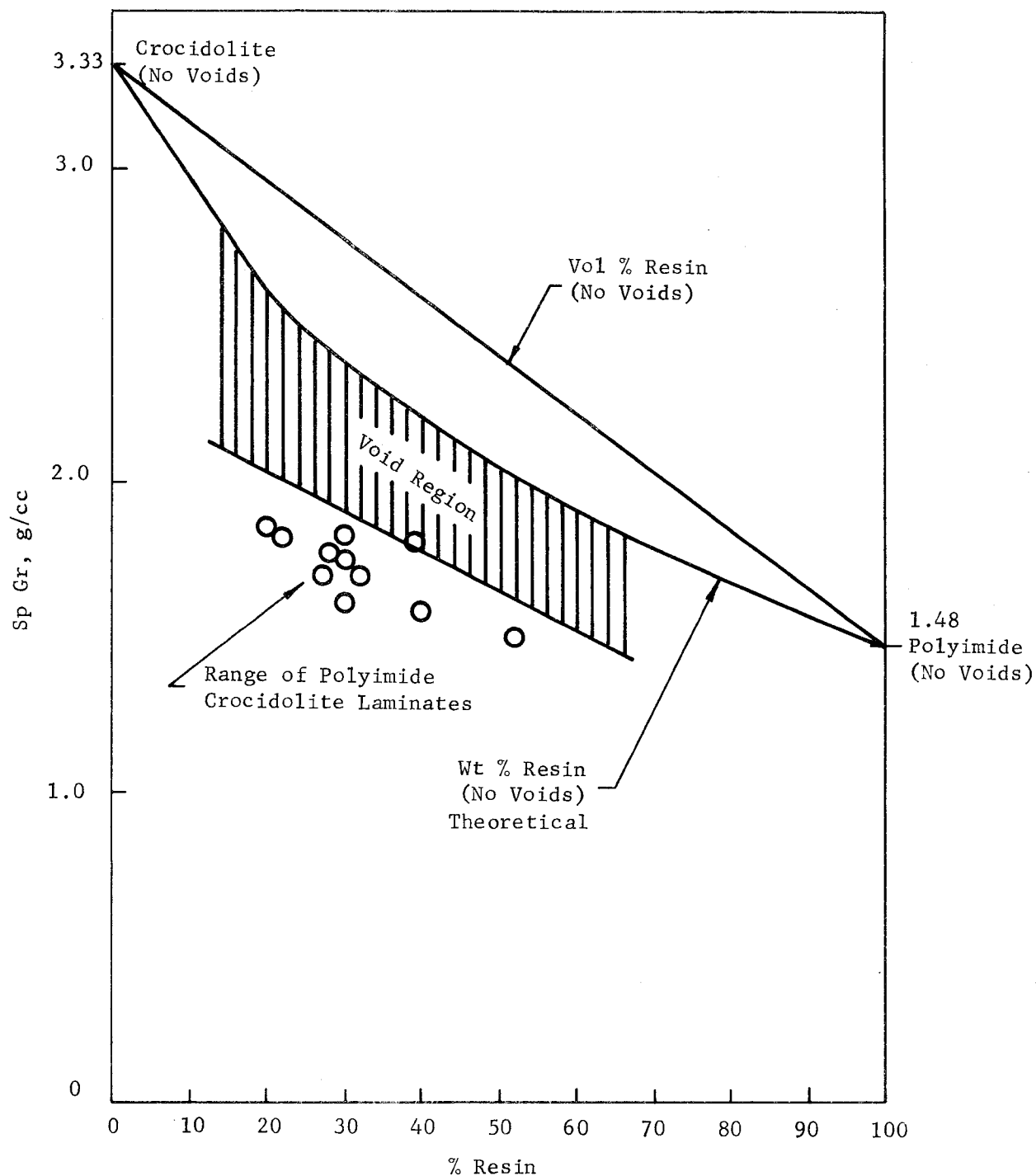
Figure 7. Specific Gravity and Resin Weight and Volume Percentages for Polyimide Cro- cidolite Laminates. The points plotted are weight percent resin and departures from theoretical illustrate the large percentage of voids

31

DISCUSSION

From the studies conducted thus far, it was concluded that Amercoat C10-G15 crocidolite mat is a superior reinforcement when laminated with Skybond 700. The thermal stability and oxidation resistance at 600°F appeared excellent.

The inability to raise the mechanical properties of these laminates through broad changes in process optimization studies appeared first to be a drawback inherent with the polyimide system. It appeared to be associated with a copius evolution of volatiles (22.9% by weight) during imide formation during cure, and second to be a problem associated with the wetting of asbestos fibers with resin.

JOINT ASBESTOS/POLYIMIDE EFFORTS

Joint efforts aimed at new approaches to the materials/processing problem were made by Narmco, Raybestos-Manhattan and Monsanto. The Monsanto group prepregged the Amercoat C10-G15 crocidolite asbestos mat with Skybond 700 and also with Skybond 701, laminated it by a wide variety of different processes, and tested the resulting laminates. They reported ultimate flexural strength properties at room temperature ranging from 23,000 psi to 29,000 psi. This does not represent any improvement over the Narmco results reported earlier. The range in Monsanto process variables is as follows:

Impregnating Resin:	50% solids
Saturation Time:	30 minutes to overnight
Drying Conditions:	Overnight at 140°F under full vacuum
Resin Pickup:	64%-76%
Volatiles:	15%-28%
Flow:	26%-54%
Cure Temperature:	350°-700°F
Cure Pressure:	25 psi-9000 psi
Laminate Resin Content:	50%
Laminate Plies:	10
Postcure:	None

Preliminary data obtained from Raybestos-Manhattan's Novabestos 7501-P asbestos/polyimide product after lamination and testing did not offer any processing or mechanical properties advantages.

32

SECTION IV

FUNDAMENTAL ASBESTOS STUDIES

To provide a better understanding of the processing required to overcome problems of wetting asbestos with resin, the potential of crocidolite reinforcement was assessed, the reinforcement potential of partially opened crocidolite ore was evaluated, and the indication of potential for oriented asbestos fibers was ascertained. This work was conducted concurrently with processing studies aimed at upgrading composite technology. Included were asbestos wetting, fiber opening, and fiber orientation experiments. The high degree of surface activity of asbestos was considered to be a probable source of the present difficulty. Note the relative comparisons of fiber diameters in Figure 8.

1 mil   1 micron   1 angstrom unit

0 . 0 0 1 , 0 4 0 , 0 0 4

Decimal Order of Magnitudes

Boron Fiber Diameter, 5 mils

1 mil

Glass Fiber, 0.2 mil

1 micron

ASBESTOS FIBER   0.004 mil (1/50th glass fiber)

Atomic Sizes, 10^{-5} to 10^{-6} mils (C-C bond = 1.5 Å)

Figure 8. Comparative Fiber Order of Magnitudes

POTENTIAL OF CROCIDOLITE REINFORCEMENT

Compression data were obtained for DEN 438/MNA/DMP-30 encapsulated crocidolite ore to assess the ultimate reinforcement potential of the fiber. The ore specimen is shown in Figure 9. Encapsulation, depicted in the sketch accompanying Table XVI was intended to prevent buckling of individual outer fibers during compression. Stress-strain relationships were determined for the resin matrix and the encapsulated specimens. From these data, the fiber modulus was calculated to be 43.8×10^6 psi, as shown in Table XVI. The present reported modulus of elasticity for crocidolite asbestos fibers is 27.1×10^6 psi. The tested compression specimens are shown in Figure 10. Crocidolite exhibited superior reinforcement potential.
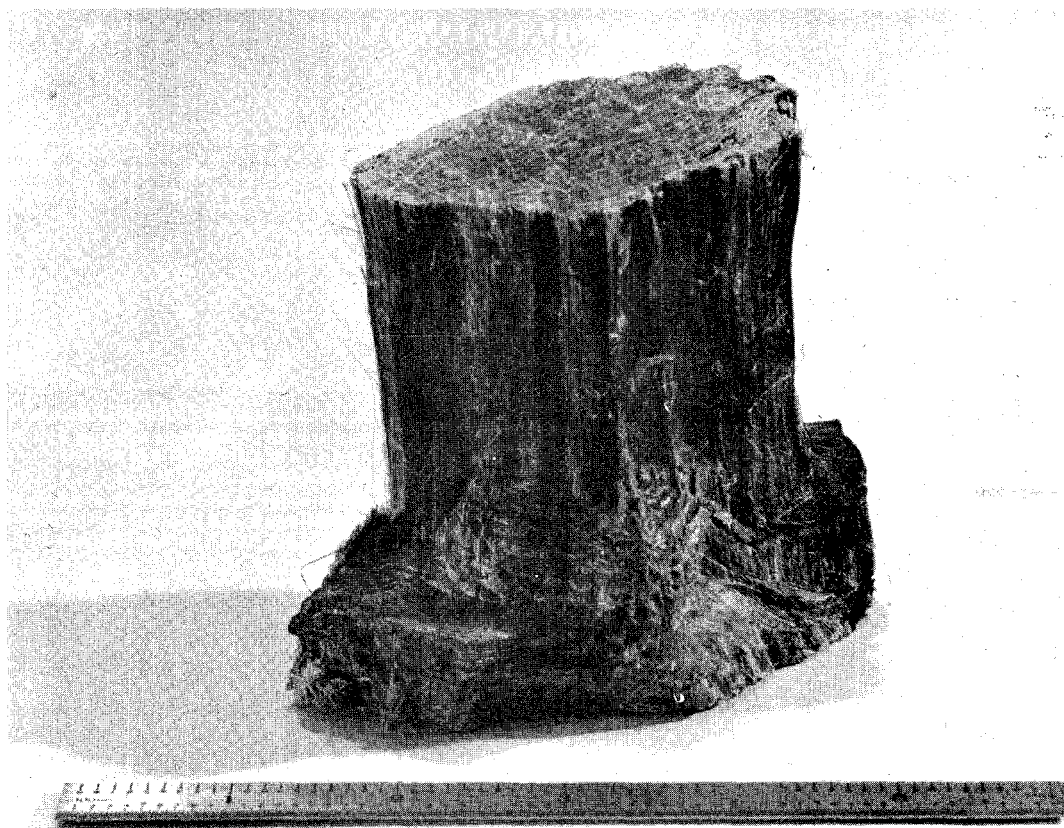

Figure 9.   Crocidolite Asbestos Ore Showing
            Undisturbed Virgin Fibers Having
            Lengths to 2 inches

TABLE XVI

COMPRESSION PROPERTIES OF COMPOSITES BASED ON
CROCIDOLITE ASBESTOS ARE* ENCAPSULATED IN AN EPOXY RESTIN MATRIX

Specimen No.	A_c	E_c, psi $\times 10^6$	A_f	A_r	E_r, psi $\times 10^6$	E_f, psi $\times 10^6$ (Calculated)
2	1.0	2.0	0.031	0.969	0.76	40.4
3	1.0	2.5	0.041	0.959	0.76	43.8

* Unopened, undisturbed crocidolite asbestos fiber
  bundles stripped from ore.

Specimen Configuration:

Unopened crocidolite
fiber bundle (approxi-
mately 1/8-3/16 inch
diameter)

1-in. OD x 1-in.
high; cast epoxy

NOTES: Formula used in calculations:

$$A_c E_c = A_f E_f + A_r E_r$$

$$E_f = \frac{A_c E_c - A_r E_r}{A_f}$$
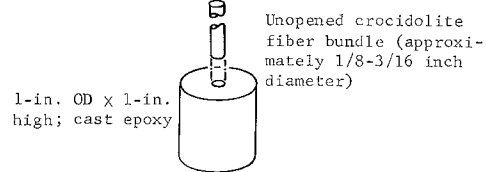
where

A_c = area fraction of composite (equal 1.000)

E_c = modulus of composite (determined)

A_f = area fraction of composite (determined)

E_f = modulus of fiber (calculated)

A_r = area fraction of resin (determined)

E_r = modulus of resin (determined)

Resin Matrix: DEN 438/MNA/DMP-30,100/101/0.75, respectively (Sp gr 1.24).

Cure: 3 hours at 200°F, 1 hour at 300°F.

Figure 10. Crocidolite Ore Specimens Encapsulated
            in an Epoxy Matrix, Shown after Com-
            pression test. Specimen 1 is a con-
            trol specimen of epoxy resin; Specimens
            2 and 3 show the continuous long fiber
            crocidolite asbestos ore

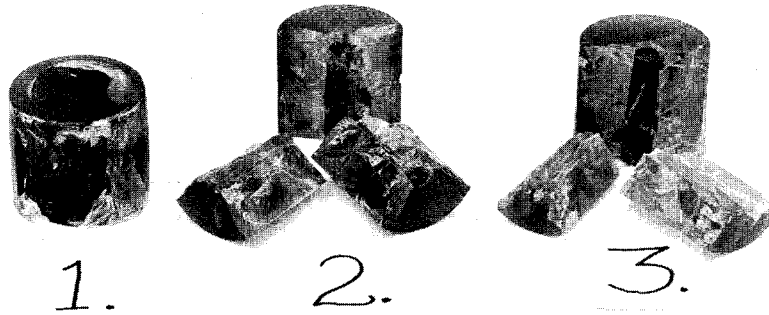The specific gravity of crocidolite was determined to be 3.33 (literature reports 3.2-3.3). We concluded that the ore in an undisturbed state had essentially zero volume void that could be impregnated with a resin matrix.

REINFORCEMENT WITH PARTIALLY OPENED CROCIDOLITE ORE

An epoxy matrix was reinforced at two loading levels, with partially opened crocidolite ore consisting of continuous length fiber bundles. Compression data indicated that these fibers could improve the pure matrix modulus by approximately 264.0% and 772.0% when used at 16.6 and 42.2 weight percent, respectively. Table XVII and Figure 11 give the details and show the results of this study. The yield failure explains the high ultimate compressive strength of the reference specimen.

TABLE XVII

COMPRESSION EVALUATION OF PARTIALLY OPENED
CROCIDOLITE ORE IN AN EPOXY MATRIX

Specimen No.	Asbestos L/D & Fiber Condition*	Wt Percent		Ult Compressive Strength, psi	Compressive Modulus psix10^6	% Improvement in Modulus	Comments
		Asbestos Fiber	Resin Matrix				
--	Control (No fiber)	0	100	40,200 48,100 44,400 46,750 44,860	0.518 0.494 0.499 0.487 0.500	Reference data	Yield & shatter failure
10	Large L/D, continuous long fiber	16.6	83.4	39,500 35,200 37,350	1.820 1.820 1.820	264.0	Shatter failure
11	Large L/D, continuous fiber	42.2	57.8	51,800 46,400 49,100	4.720 4.010 4.360	772.0	Shatter failure

* Crocidolite fibers were stripped continuous length from the ore
  to form bundles of approximately 0.025-in. diameter.

NOTES: Resin Matrix: DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively (Sp gr 1.24).

    Cure: 3 hours at 200°F
          1 hour at 300°F
          1 hour at 400°F

    Specimen Configuration and Testing: ASTM D-695 (1/2 in. x 1/2 in. x 1 in.).

Fiber Orientation:

36
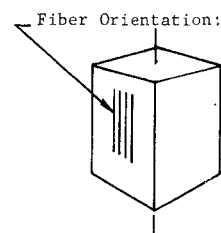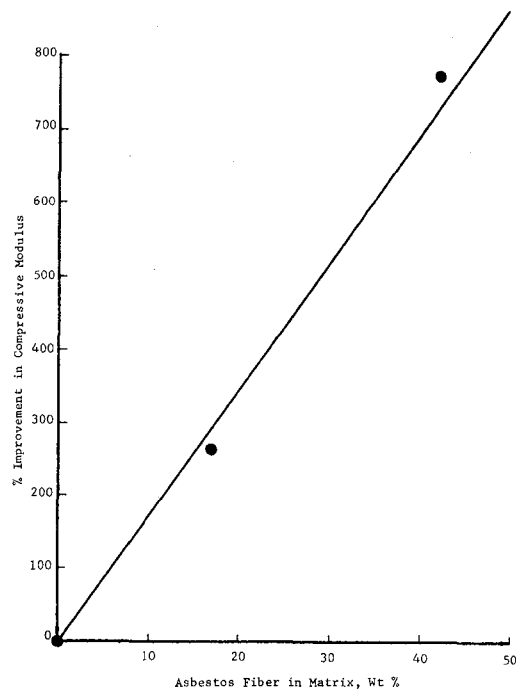
Figure 11.   Improvement in Compressive
             Modulus Resulting from Vari-
             ous Additions of Partially
             Opened Crocidolite Ore to
             an Epoxy Matrix

INDICATION OF POTENTIAL OF ORIENTED ABESTOS FIBER

    A study was made of two reinforcement parameters: oriented as compared
with random fibers, and both large and small L/D fiber ratios. Commercially
opened virgin crocidolite fiber was used to prepare compression specimens by
an inventory procedure to control the weight percent at 8.85. Orientation
was accomplished by a hand "taffy pull" procedure prior to loading the mold
cavity for comparison with specimens made with random fiber. Compression
data are shown in Table XVIII. Oriented fiber and large fiber L/D ratios
were proven to be superior over random orientation and small L/D ratios.

    This work indicated that extrusion of asbestos fibers in a resin matrix
would affect alignment or orientation, but 5 weight percent fiber was the
limiting amount. More than this amount of fiber rendered this matrix too
viscous or thixotropic to extrude. No further efforts were expended on
extrusion as a means for fiber alignment.

TABLE XVIII

COMPRESSION EVALUATION OF ORIENTED AND RANDOM
CROCIDOLITE VIRGIN FIBER* HAVING VARYING L/D RATIOS

Specimen No.	Asbestos L/D & Fiber Condition	Sp Gr	Wt Percent		Vol % Void	Ult Compressive Strength† psi	Compressive Modulus psi$\times 10^6$	% Improvement in Modulus
			Asbestos Fiber	Resin Matrix				
12	Large L/D long fiber, oriented**	1.19	8.85	91.15	9.23	23,700 23,200 24,000 23,200 23,500	0.904 0.880 0.880 0.865 0.882	67.0
16	Large L/D, long fiber, random	1.20-1.25			7.04	11,600 15,100 16,400 13,900 14,300	0.412 0.568 0.597 0.536 0.528	Reference data
18	Small L/D, short fiber, oriented**	1.16-1.20	8.85	91.15	10.09	23,500 20,000 25,300 25,300 23,500	0.765 0.710 0.852 0.817 0.786	27.2
17	Small L/D, short fiber, random	1.27-1.28			2.85	18,200 18,400 22,800 17,000 19,100	0.631 0.625 0.629 0.588 0.618	Reference data

* Commercially available virgin fiber.

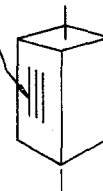** Orientation accomplished by "taffy-pull" procedure.

† Shatter type of failure.

NOTES: Resin Matrix: DEN 438/MNA/DMP-30, 100/101/0.75-pbw, respectively (Sp gr 1.24).

      Cure: 3 hours at 200°F
             1 hour at 300°F
             1 hour at 400°F

      Specimen Configuration and Testing: ASTM-D-695 (1/2 in. $\times$ 1/2 in. $\times$ 1 in.)

Fiber Orientation, Specimens 12 and 18:

ASBESTOS FIBER WETTING STUDIES

The tremendous surface area presented by asbestos fibers has been of concern in this work. In one attempt to improve wetting, carded virgin crocidolite fiber was combined with an epoxy resin matrix and subjected to hydroclaving at 29,000 psi. We anticipated that this high pressure might effect better wetting. Specimen 21 (Table XIX) is representative of the results of this study. Comparison with Specimen 16 (Table XVIII) indicated that hydroclaving produced a better modulus (0.718 versus 0.528 $\times$ 10^6 psi) at essentially the same fiber weight percent in the composite.

In another similar experiment, carded crocidolite virgin fiber was vacuum-deposited with aluminum in an attempt to alter the asbestos fiber surface characteristics and to enhance wetting. Specimen 23 (Table XVIII) reveals the results of this study. Comparison with Specimen 16 (Table XIX) indicated that a vacuum deposition of aluminum on the asbestos fiber produced a better modulus (0.726 versus 0.528 $\times$ 10^6 psi) at approximately identical fiber weight percent. At this point, we questioned whether this effect and the foregoing effect might be synergistic.

38

TABLE XIX

COMPRESSION PROPERTIES RESULTING FROM MISCELLANEOUS
ASBESTOS WETTING AND ORIENTATION STUDIES

Specimen No.	Asbestos L/D & Fiber Condition	Sp Gr	Wt Percent		Vol % Void	Ult Compressive Strength, psi	Compressive Modulus, $psi \times 10^6$	% Improvement in Modulus	Comments
			Asbestos Fiber	Resin Matrix					
21	Large L/D, virgin fiber impregnated by hydroclaving at 29,000 psi, nonoriented	1.28 1.27 1.27 1.22 1.26	7.3	92.7	3.02	20,200 21,000 21,800 15,500 19,600	0.748 0.677 0.772 0.677 0.718	43.6	Shatter failure
22	Large L/D, crocidolite ore opened by pressure rollers, oriented with butt joints & overlap layers	1.50	70.0	30.0	31.89	55,100	3.94	688.0	
23	Large L/D, virgin crocidolite fiber with vacuum deposition of aluminum, nonoriented	1.20	7.8	92.2	7.94	18,300 19,600 18,950	0.729 0.724 0.726	45.2	
24	Small L/D, crocidolite fiber and epoxy resin combined on rubber mill, nonoriented	1.95	77.6	22.4	18.91	72,400	1.84	268.0	

* Control specimen, resin matrix only, no fiber, avg compressive strength
44,860 psi and modulus 0.500 x 10^6 psi.

NOTES: Resin matrix DEN 438/MNA/DMP-30, 100/101/0.75-pbw, respectively.

Cure: 3 hours at 200°F
1 hour at 300°F
1 hour at 400°F

Specimen Configuration and Testing: ASTM D-695 (1/2 in. x 1/2 in. x 1 in.).

Fiber Orientation,
Specimen 22

A fluidized bed procedure was used to impregnate carded crocidolite virgin fiber with an ultrafine powder so that the fiber could be wetted with a controlled amount of resin. Subsequent examination showed the procedure has merit.

Early in the program, we noted the possibility existed for hydroclave impregnation of asbestos fibers to improve wetting with resin and to upgrade composite properties. A set of compression specimens was fabricated from random fiber C10-G15 Amercoat crocidolite mat, wherein 100% solids impregnation was accomplished by cycling 40 times between 0 psi and 15,000 psi to force fiber wetting. Table XX shows the results of this study. When compared with the set of control specimens where hydroclaving was not employed, no advantage could be seen for hydroclave impregnation.

TABLE XX

EFFECT OF HYDROCLAVE IMPREGNATION ON
COMPRESSION PROPERTIES OF CROCIDOLITE EPOXY COMPOSITES

(100% Solids Impregnation)

Speci-men No.	Processing	Sp Gr	Wt % Asbestos Fiber*	Wt % Resin Matrix	Vol % Void (Calc)	Vol % Resin		Vol % Asbestos (Calc)	Ult Compressive Strength, psi	Compressive Modulus, psi × 10⁶	Improvement in Modulus,** %	Comments
						Difference	Charted					
HYDROCLAVED (40 cycles 0-15,000 psi)												
43	Long L/D, Random fiber 5000-psi molding pressure	2.16	71.9	28.1	4.41	46.80	52.0	48.79	41,500 27,500 34,500	3.97 2.29 3.13	526.0	Shatter type of failure
CONTROL (No Hydroclaving)												
25	Same as above, except 1250-psi molding pressure	1.99	60.2	39.8	0.17	63.80	64.0	36.03	36,800***	3.52	604.0	Shatter type of failure
27	Same as above, except 2500-psi molding pressure	2.12	64.9	35.1	1.31	57.92	59.0	40.77	37,200***	3.90	680.0	Shatter type of failure
28	Same as above, except 5000-psi molding pressure	2.37	76.6	23.4	0.77	44.30	46.0	54.93	32,400***	3.90	680.0	Shatter type of failure

  * By difference.

 ** Control specimen, resin matrix only, no fiber, avg ult compressive strength 44,860 psi, and modulus 0.500×10^6 psi.

*** Avg of four specimens.

NOTE: Resin matrix DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively.
       Cure: 3 hr @ 200°F
             1 hr @ 300°F
             1 hr @ 400°F
       Crocidolite asbestos mat: Amercoat C10-G15.
       Specimen configuration and test: ASTM D-695 (1/2 in. × 1/2 in. × 1 in.)

40

Several new attempts were made to coat the asbestos fibers with metal to afford an improved surface for wetting by resin. The first attempt involved wetting with molten aluminum and various low-melting aluminum alloys. The results were negative; no wetting could be attained. The second involved an electroless solution deposit of copper on the asbestos fibers. The results were positive, but poor uniformity and shallow plating made the technique impractical.

ASBESTOS FIBER OPENING STUDIES

Although the reinforcement potential for crocidolite ore has been established, opening of the ore into a fiber array is necessary for the fabrication and processing of reinforced plastic hardware. Some degrees of openness of the ore and fiber length have been evaluated in the foregoing work. The following additional studies were also conducted.

A process was evaluated for parallel opening of the bundles of crocidolite fibers by passing them with axes at right angles to the axis of the pressure rolls.* The result was an excellent degree of opening into a fiber array, with the added advantages of unidirectional orientation and continuous long fibers. Impregnation with epoxy resin was accomplished by transferring the parallel array to a cast film of epoxy resin. Data for Specimen 22 (see Figure 12) (Table XIX) demonstrate the results of this effort. The molded specimen contained lapped and butted fibers. A compressive modulus of 9.94×10^6 psi was good, representing a 688.0% improvement over that of the nonreinforced resin matrix at a fiber weight percent of 70.0. The modulus improvement over random orientation (Specimen 24) was 257%.
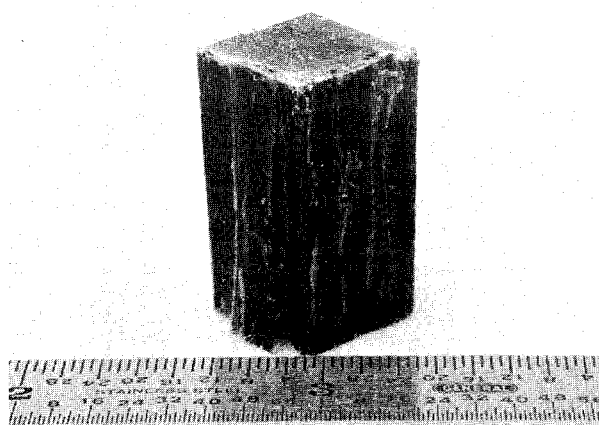

Figure 12. Tested Compression Specimen 22 Consisting of a 70 Weight Percent Oriented Asbestos Fiber Array in an Epoxy Matrix

* H. Berger and R. E. Oesper, Asbestos with Plastics and Rubber, p 24 (Also Swiss Patent No. 277,086 and US Patent No. 2,640,797, with English priority from 1948-1949).

Specimen 24 (Table XIX) represents an attempt to maximize the degree of opening of the fiber. Carded virgin crocidolite fiber was added to an epoxy resin by mixing on a rubber mill. The resulting L/D was small and the asbestos weight percent high. The compressive modulus was only 268.0% better than that of the nonreinforced resin matrix.

Fiber bundles were also subjected to liquid nitrogen in an attempt to freeze the inherent absorbed water in the asbestos and split the bundles into a fine fiber array. No opening of the bundles was observed.

Other bundles were subjected to ultrasonic energy (54.0 kilocycles) to open them into a fiber array. This procedure was equally ineffective.

One method which was effective in opening bundles was to expose sealed glass ampoules of water-saturated fiber bundles to 1000°F so that the ampoule would explode. The resultant opened fiber array, however, was badly oriented.

ASBESTOS FIBER ORIENTATION STUDIES

It has already been implied that asbestos fibers could be oriented for maximum reinforcement by extrusion or "taffy-pull" techniques in a resin matrix. Other studies were conducted along these lines in order to take advantage of the maximum reinforcement potential of asbestos fibers. Commercial sources of oriented asbestos fiber mat, paper, and fabric were sought for structural advantages.

Asbestos fibers were found to be susceptible to orientation by static charges. Random fibers were placed between plates charged with 40,000 volts of direct current and were oriented perpendicular to the plates. Being nonconductive or dielectric, virgin asbestos fibers were not susceptible to orientation by a magnetic field. It is possible, however, that treatment or coating with salts or other conductive materials would render them susceptible.

Orientation of asbestos in a resin matrix at first could only be accomplished at comparatively low weight percentages (about 5% maximum), because of the thixotropic nature of the fibers, except by the pressure roll method described above. Thickening takes place, reducing the mobility of the fiber and the ability to draw or orient it.

An experimental quantity of asbestos fiber reinforced filaments was ordered from the Carborundum Company. These filaments, similar to the silicon carbide whisker filaments offered by this company, consist of oriented whiskers in a acrylonitrile resin matrix. These filaments can be used as building blocks in composite fabrication where the binder is ignited and the oriented whiskers are reconstituted with the desired resin matrix. Narmco supplied the virgin crocidolite fiber, which Carborundum chopped to 40-100 mil length, combined with binder, and produced oriented asbestos fiber reinforced filaments in lengths up to 2 feet. The filaments had an average of only 3.0 weight percent asbestos fiber after ignition at 1050°F. Because this ignition temperature could cause severe degradation to the asbestos, an ignition temperature of 500°F was tried. Weight loss after 2 hours at 500°F in air was only 12.0%. The resinous residue was heavily carbonaceous, and this ignition temperature not considered practical.

Specimens 19 and 20 (Table XXI) are representative of the compression data that were obtained from bonding the Carborundum asbestos fiber reinforced filaments in an epoxy matrix without removal of binder and after ignition at 1050°F, respectively. The modulus improvement to the resin matrix was 16 and 20%, respectively. These percentages are considered to be quite good for such a low asbestos fiber loading level (3-4 weight percent). Attempts were made to increase composite density and fiber content by igniting a thin layer of filaments, reconstituting with epoxy resin, and building up in the mold cavity. This technique has not yet been successful because of the directional instability of the asbestos fiber filaments in thin layers.

TABLE XXI

COMPRESSION PROPERTIES OF ORIENTED CROCIDOLITE ASBESTOS
FIBER FILAMENTS* IN AN EPOXY MATRIX

| Specimen No. | Asbestos L/D & Fiber Condition | Sp Gr | Wt Percent | | Vol % Void | Ult Compressive Strength, psi | Compressive Modulus, psix10⁶ | % Improvement in Modulus** | Comments |
			Asbestos Fiber	Resin Matrix					
19	Small L/D, chopped (40-100 mils), oriented in acrylonitrile binder	1.08	3.1	96.9	14.59	16,700 17,100 17,200 16,500 16,900	0.575 0.593 0.594 0.562 0.581	16.2	Shatter failure
20	Small L/D, chopped (40-100 mils), oriented, ignited 1000°F and reconstituted with epoxy	1.23	4.2	95.8	3.41	19,100	0.603	20.6	

* Asbestos fiber reinforced filaments produced by Carborundum Company, New Products Division, Niagara Falls, New York, containing 3 percent asbestos and 97 percent acrylonitrile binder.

** Control specimen, resin matrix only, no fiber, avg ult compressive strength 44,860 psi, and modulus 0.500 x 10⁶ psi.

NOTES: Resin Matrix: DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively.

Cure: 3 hours at 200°F
1 hour at 300°F
1 hour at 400°F

Specimen Configuration and Testing: ASTM D-695 (1/2 in. x 1/2 in. x 1 in.).

Fiber and Filament Orientation
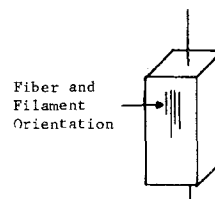
SCREENING OF PROCESSING METHODS

Asbestos fibers have been used as the acceptors during a radio frequency (450 kilocycles) induction heating experiment in an attempt to find improved processing techniques. Because of the dielectric properties of virgin asbestos, however, the fibers are not susceptible to induction heating. Suitable coatings might overcome this deficiency.

COMPOSITE COMPOSITION STUDIES, NONORIENTED FIBER

Initial studies indicated the excellent reinforcement potential of crocidolite asbestos. We concluded from these studies that reinforcement was a direct function of fiber weight percent in the composite. Furthermore, we anticipated that there was probably an optimum fiber and resin matrix composition for best reinforcement, and that optimization occurred at minimum composite void content.

43

A series of composition studies was undertaken, based on C10-G15 Amercoat random fiber crocidolite asbestos mat because of its ready availability. One-hundred percent solids and also methyl ethyl ketone solution impregnations were employed in an inventory procedure for varying the resin weight percent in the composite between approximately 10 and 40. Solution impregnation was accomplished by saturating the asbestos mat in 10%-30% solids (depending on inventory amount desired in composite specimen) solution of epoxy resin in methyl ethyl ketone. An oven dry of 30 minutes at 180°F followed this procedure to expel the solvent.

The 100% solids impregnations were expected to reduce void content of composites by minimizing volatiles; the solution impregnations were expected to afford improved fiber wetting. Compression specimens (ASTM-D-695) were prepared by compression molding the impregnated mat between pressures of 1250-5000 psi.

Table XXII gives the processing particulars and physical and mechanical properties for the resultant composites. An 876.0% improvement in modulus was afforded the resin matrix by 75.3 weight percent random fiber asbestos at a low void content of 1.21 volume percent. Figure 13 shows the resin weight and volume versus specific gravity relationship. It is very interesting to note that all composites have very low void content. Offsets from the theoretical weight percent curve indicate percentage void. Figure 14 was prepared to assist in the analysis of the data in Table XXII and in the optimization processing of C10-G15 crocidolite asbestos mat and epoxy composites.

COMPOSITE COMPOSITION STUDIES, ORIENTED FIBERS

To augment studies already completed on C10-G15 Amercoat random fiber crocidolite asbestos mat, we initiated a composition study based on oriented crocidolite fiber. Once again, 100% solids and also methyl ethyl ketone solution impregnations were employed in an inventory procedure for varying the resin weight percent in the composite between approximately 10 and 40. The 100% solids impregnations were expected to reduce void content of the composites by minimizing volatiles; the solution impregnations were expected to afford improved fiber wetting. Figure 15 shows fabrication of an oriented crocidolite fiber epoxy prepreg supported by Mylar film.

Solution impregnation was accomplished by saturating the asbestos fiber arrays while maintaining orientation in 10%-30% solids (depending on the inventory amount desired in the composite specimen) solution of epoxy resin in methyl ethyl ketone. An oven dry of 30 minutes at 180°F followed this procedure to expel the solvent.

Compression specimens (ASTM-D-695) were prepared by compression-molding the resultant prepregs between pressures of 100 psi and 5000 psi.

Table XXIII shows the processing and results of these studies. Figure 16 is a correlation between resin weight and resin volume percentages and specific gravity. The plotted specimens are close to theoretical weight percent of resin, indicating extremely low composite void contents. A buckling failure at the end planes was experienced in testing the 100% solids impregnations. To attain compression failure in the middle of the specimen, the ends of the solution coated specimens were reinforced as shown in Figure 17.

44

TABLE XXII

RESIN CONTENT OPTIMIZATION FOR CROCIDOLITE MAT — EPOXY COMPOSITES BASED ON 100% SOLIDS AND SOLUTION IMPREGNATIONS

Specimen	Processing	Sp Gr	Wt % Asbestos Resin Fiber	Wt % Asbestos Resin Matrix	Vol % Void (Calc)	Vol % Resin Calc	Vol % Resin Charted	Vol % Asbestos (Calc)	Ult Compressive Strength, psi	Compressive Modulus, psi x 10^6	% Improvement in Modulus*	Comments
						100% SOLIDS IMPREGNATION						
25	Long L/D, random fiber, 1250 psi molding pressure	1.99	60.2	39.8	0.17	63.80	64.0	36.03	36,200 39,600 32,600 <u>38,700</u> 36,800	3.60 3.63 3.44 <u>3.39</u> 3.52	604.0	Shatter type failure
27	Long L/D, randome fiber, 2500 psi molding pressure	2.12	64.9	35.1	1.31	57.92	59.0	40.77	36,400 37,100 38,200 <u>37,000</u> 37,200	3.89 3.76 3.63 <u>4.33</u> 3.90	680.0	
28	Long L/D, random fiber, 5000 psi molding pressure	2.37	76.6	23.4	0.77	44.30	46.0	54.93	32,400 33,000 33,100 <u>31,100</u> 32,400	3.60 4.03 4.25 <u>3.72</u> 3.90	680.0	
						SOLUTION IMPREGNATIONS						
34	Long L/D, random fiber, 5000 psi molding pressure	2.31	83.0	17.0	10.76	24.73		64.51	10,300 12,300 13,000 <u>11,100</u> 11,700	2.28 2.35 2.43 <u>2.52</u> 2.40	380.0	Shatter type failure
31	Long L/D, random fiber, 5000 psi molding pressure	2.38	75.3	24.7	1.21	45.63	46.0	53.16	35,400 36,300 37,200 <u>36,300</u> 36,300	5.16 4.57 4.62 <u>5.17</u> 4.88	876.0	
32	Long L/D, random fiber, 2500 psi molding pressure	2.07	64.2	35.8	0.34	59.63	60.0	40.03	37,800 34,500 39,000 <u>37,800</u> 37,300	3.94 4.00 4.18 <u>4.10</u> 4.06	713.0	
33	Long L/D, random fiber, 1250 psi molding pressure	2.02	2.02	38.2	0.29	62.12	62.0	37.59	38,500 34,900 40,000 <u>39,200</u> 38,200	3.85 3.78 3.78 <u>3.70</u> 3.78	656.0	

* Control specimen, resin matrix only, no fiber, average compressive ultimate 44,860 psi and modulus 0.500 x 10^6 psi.

Resin matrix DEN 438/MNA/DMP-30, 100/101/0.75

Cure: 3 hr @ 200°F
1 hr @ 300°F
1 hr @ 400°F

Specimen configuration and testing: ASTM D-695 (½ in. x ½ in. x 1 in.)

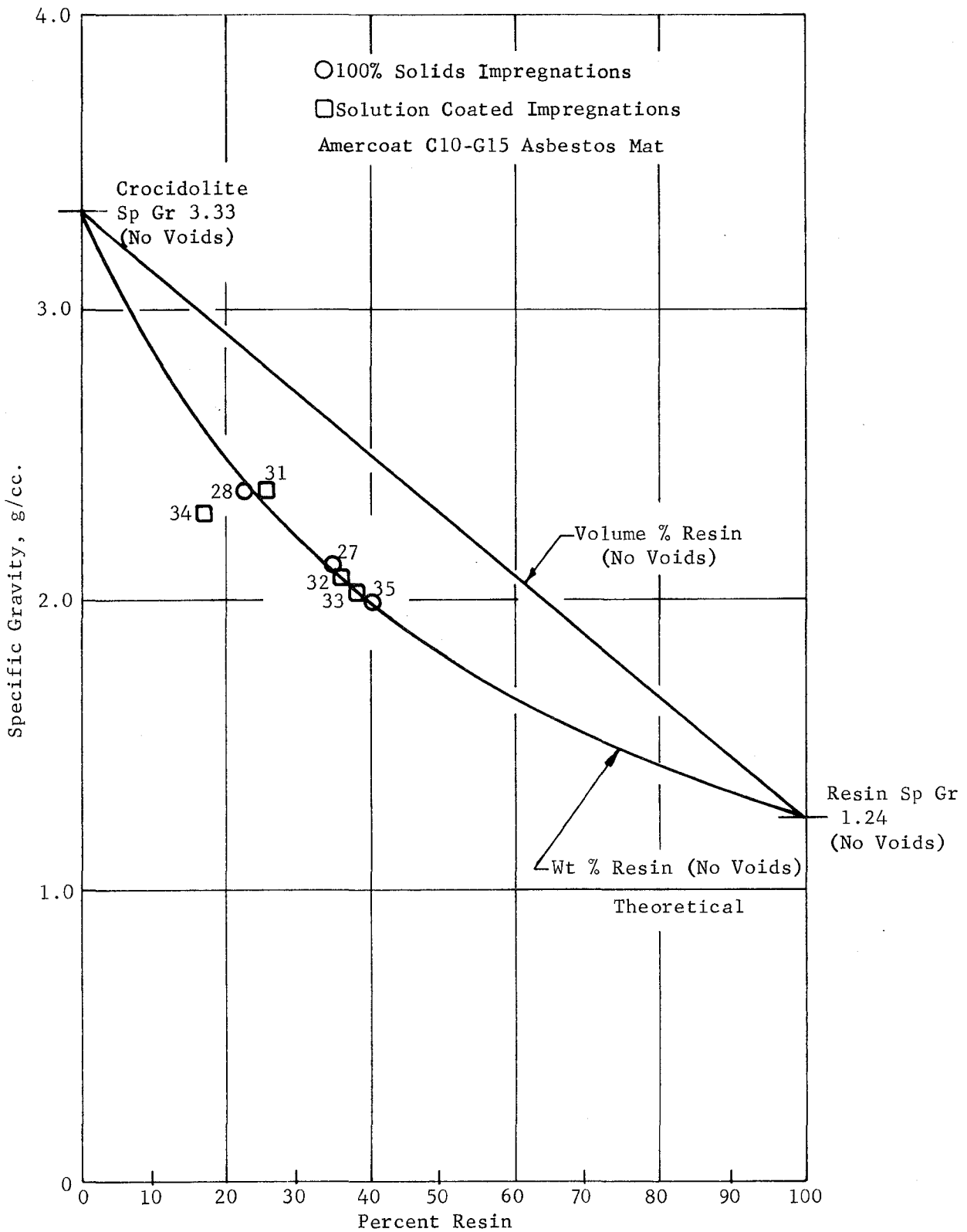Crocidolite asbestos mat: Amercoat C10-G15
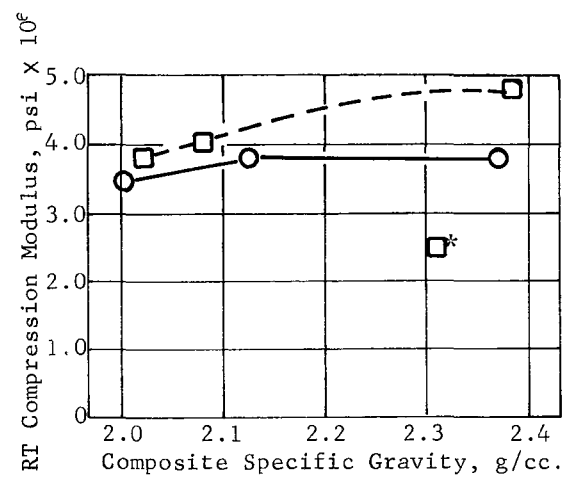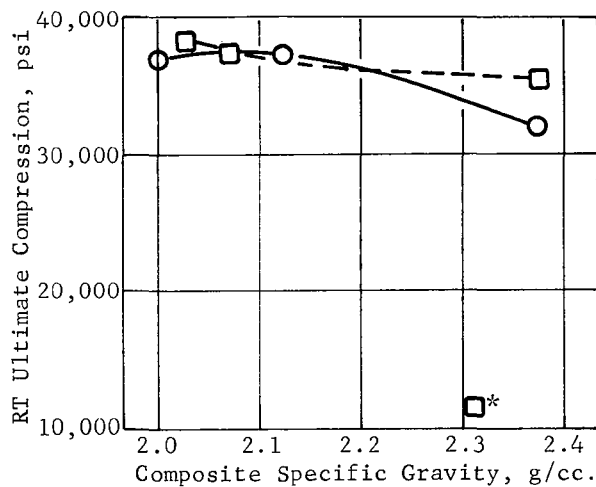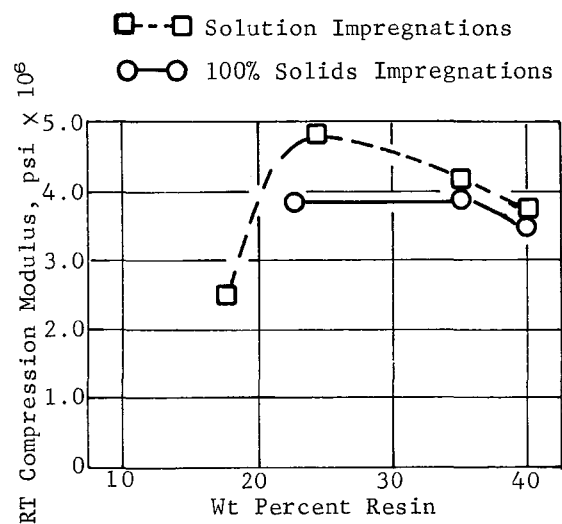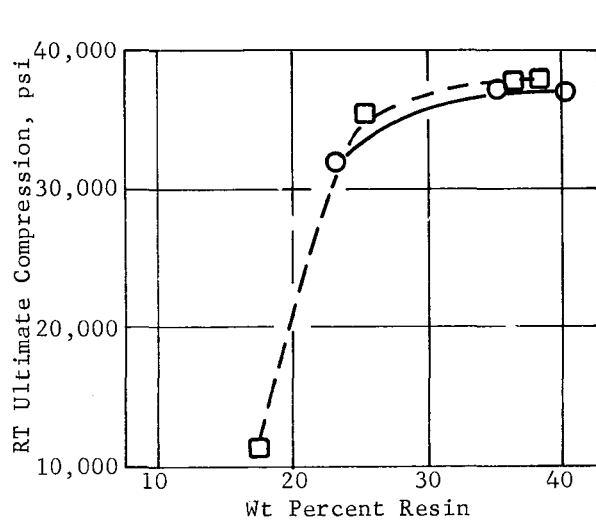
Figure 13.   Relationship Between Composite Specific Gravity
            and Percent Resin by Weight and Volume. The
            points are weight percent resin.

46
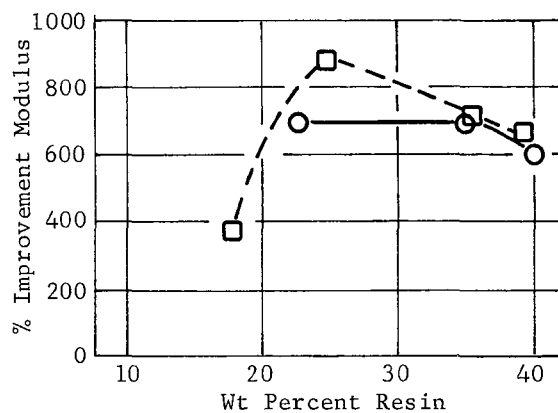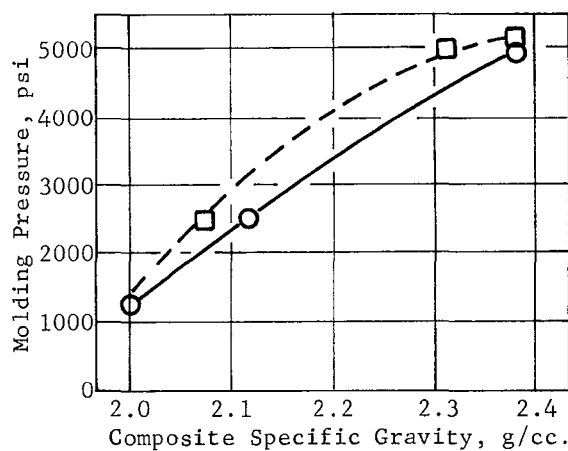
Figure 14. Physical and Mechanical Properties Relationships for
Amercoat C10-G15 Crocidolite Mat and Epoxy Matrix
Composites

47
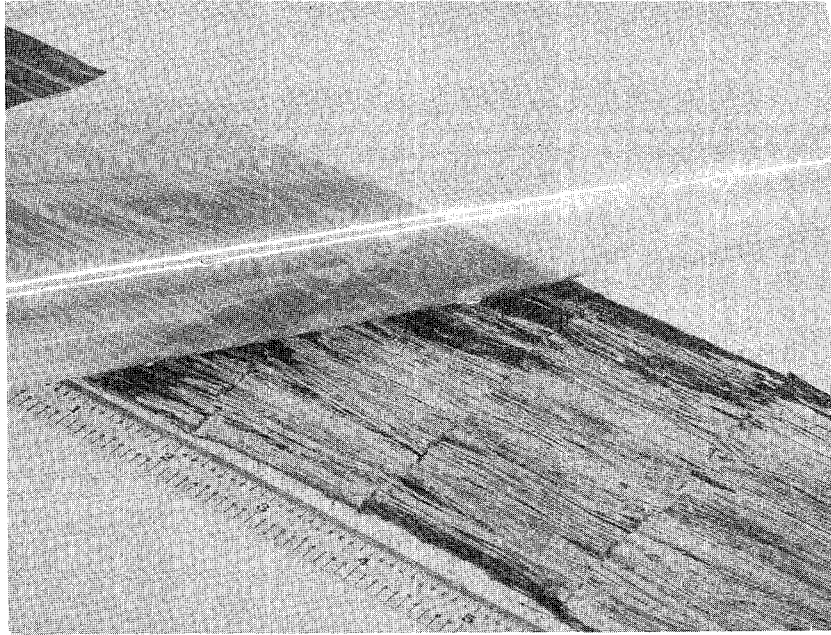
Figure 15.   An Oriented Crocidolite Asbestos Tape
             Consisting of a Fiber Array Resulting
             from Bundles Passed at Right Angles
             between Pressure Rolls. The array of
             fibers has been laid parallel on a
             portion of a controlled amount of
             epoxy resin coated on Mylar film.
             The remaining controlled portion of
             resin has been coated on the Mylar
             film which will be used to cover
             the tape to complete the impregna-
             tion

TABLE XXIII

RESIN CONTENT OPTIMIZATION FOR ORIENTED CROCIDOLITE FIBER — EPOXY COMPOSITES BASED ON 100% SOLIDS AND SOLUTION IMPREGNATIONS

Speci-men No.	Processing	Sp Gr	Wt % Asbestos Fiber*	Wt % Resin Matrix	Vol % Void (Calc)	Vol % Resin Difference	Vol % Resin Charted	Vol % Asbestos (Calc)	Ult Compressive Strength, psi	Compressive Modulus, psi × 10^6	Improvement in Modulus,** %	Comments
					100% SOLIDS IMPREGNATION (Std Specimen)							
35	Long L/D Oriented fiber 5000-psi molding pressure	2.80	83.1	16.9	8.03	27.30	34.0	64.67	18,300 34,400 26,350	2.34 3.14 2.74	446.0	Buckling failure
36	Same as above, except 100-psi molding pressure	2.07	57.8	42.2	6.37	59.86	66.0	33.77	70,100 58,300 64,200	5.56 5.56 5.56	1001.0	Buckling failure
37	Same as above, except 1250-psi molding pressure	2.10	60.3	39.7	5.26	58.62	64.0	36.12	36,300 34,900 35,600	6.00 6.25 6.12	1130.0	Buckling failure
					SOLUTION IMPREGNATIONS (Specimen Ends Reinforced)							
38	Same as above, except 5000-psi molding pressure	2.88	90.9	9.1	0.24	20.95	16.0	78.81	71,400 58,400 64,900	13.5 21.7 17.6	3420.0	Normal compression failure
39	Same as above, except 1250-psi molding pressure	2.36	72.6	27.4	3.60	46.74	50.0	49.66	112,200 92,900 102,600	8.23 2.17 5.20	938.0	Normal compression failure
40	Same as above, except 100-psi molding pressure	2.01	65.8	34.2	4.84	53.43	58.0	41.73	79,200 73,400 76,300	1.99 8.77 5.38	980.0	Normal compression failure

* By difference.

** Control specimen, resin matrix only, no fiber, avg ult compressive strength 44,860 psi, and modulus 0.500 × 10^6 psi.

NOTE: Resin matrix DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively.
Cure: 3 hr @ 200°F
1 hr @ 300°F
1 hr @ 400°F
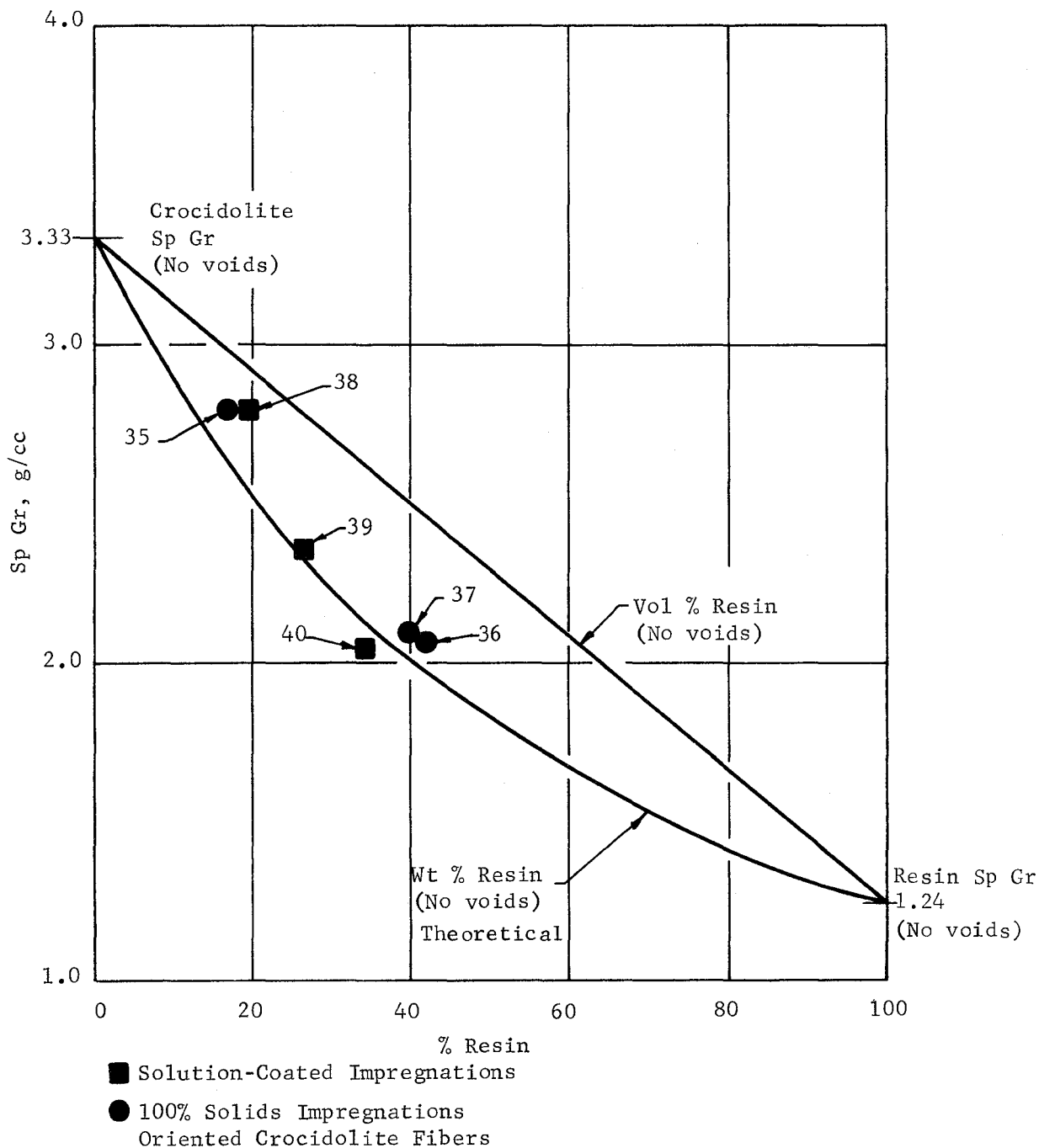Specimen configuration and test: ASTM D-695 (1/2 in. × 1/2 in. × 1 in.)

Figure 16. Relationship between Composite Specific
Gravity and Percent Resin by Weight and
Volume. The plotted specimens are close
to theoretical zero void and represent
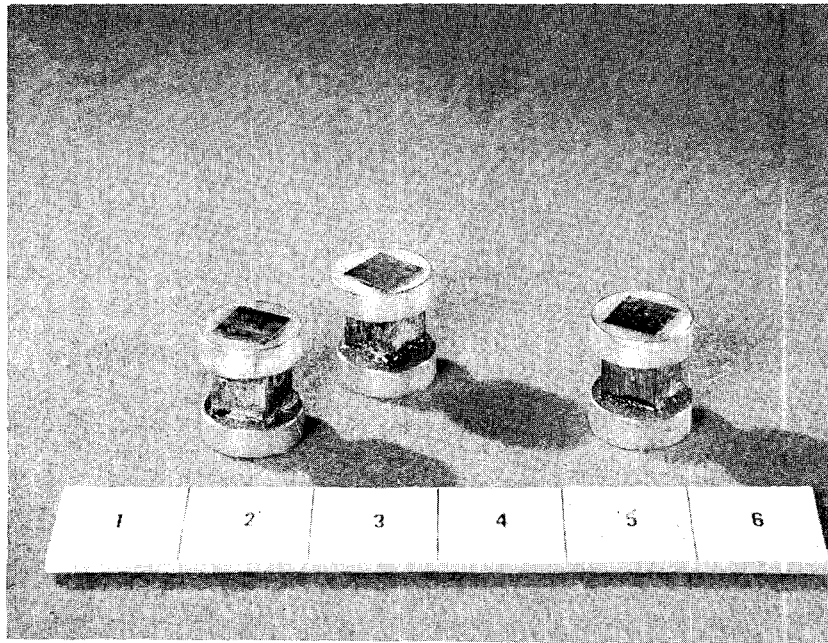weight percent resin

Figure 17. Ends of Oriented Crocidolite Epoxy
Compression Specimens (ASTM D-695)
Reinforced to Prevent Buckling
Failure. Specimens are Nos. 38,
39, and 40

Figure 18 was compiled to assist in the analysis of the data in Table XXIII and in the optimization processing of oriented crocidolite asbestos fiber and epoxy composites. The 100% solids and solution impregnations represent different specimens; nevertheless, there is every indication that the modulus of the specimens is extremely sensitive to the efficiency of fiber support. A buckling type of compression failure occuring at low resin content and high density can be expected to result in marginal or low ultimate compressive strength and modulus data. Reinforcement of specimens overcomes this sensitivity, as would be expected. There is considerable range in values for the two data points; nevertheless, the highest data point should be considered in assessing the potential for the systems. The arithmetic mean data may be misleading in determining the available potential.

A modulus improvement of 3,420% over the resin matrix, and an ultimate compressive strength of 112,200* psi and modulus 21.7 X 10^6** psi is inherent in oriented crocidolite epoxy composites. High (5,000 psi) molding pressures, high density (2.75 g/cc), and low resin content (9.0 weight percent) appear to be an approach to optimum.

BLEND OF RANDOM AND ORIENTED CROCIDOLITE FIBERS TO UPGRADE LOAD TRANSFER CHARACTERISTIC COMPOSITES

Table XXIV shows the results of a study whose objective was to upgrade load transfer characteristics in crocidolite epoxy composites by blending 50 weight percent oriented with 50 weight percent random (C10-G15 Amercoat mat) reinforcement. We anticipated that this would reduce the sensitivity of the asbestos fiber to support. When compared with controls consisting of 100 weight percent oriented and also 100 weight percent random fiber, the ultimate compressive strength was upgraded and the compressive modulus was not improved at comparable resin contents and densities.

---

* Specimen 39, Table XXIII, p. 49.
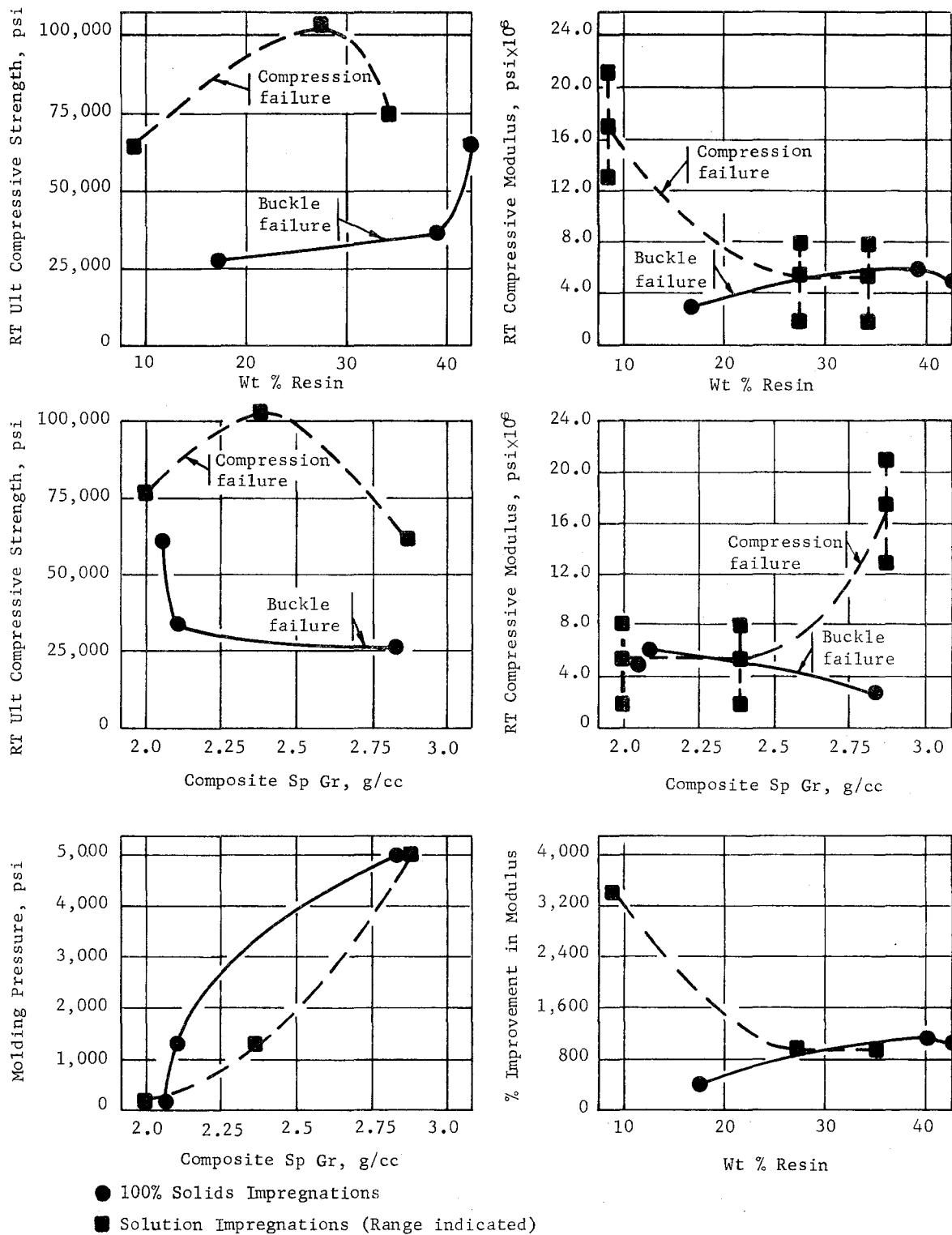** Specimen 38, Table XXIII, p. 49.

Figure 18. Physical and Mechanical Properties Relationships for Crocidolite Oriented Fiber and Epoxy Matrix Composites

TABLE XXIV

BLEND OF RANDOM AND ORIENTED CROCIDOLITE FIBERS
TO UPGRADE LOAD TRANSFER CHARACTERISTICS IN COMPOSITE

(100% Solids Impregnation)

Speci-men No.	Processing	Sp Gr	Wt % Asbestos Fiber*	Wt % Resin Matrix	Vol % Void (Calc)	Vol % Resin Difference	Vol % Resin Charted	Vol % Asbestos (Calc)	Ult Compressive Strength, psi	Compressive Modulus, psi x 10^6	Improvement in Modulus,** %	Comments
						CONTROL (Random Fiber)						
25	Long L/D, Random fiber 1250-psi molding pressure	1.99	60.2	39.8	0.17	63.80	64.0	36.03	36,800***	3.52	604.0	Shatter type of failure
27	Same as above, except 2500-psi molding pressure	2.12	64.9	35.1	1.31	57.92	59.0	40.77	37,200***	3.90	680.0	Shatter type of failure
28	Same as above, except 5000-psi molding pressure	2.37	76.6	23.4	0.77	44.30	46.0	54.93	32,400***	3.90	680.0	Shatter type of failure
						SPECIMEN ENDS REINFORCED						
44	Long L/D, Random fiber and oriented fiber, 50 wt % each 4000-psi molding pressure	2.40	74.7	25.3	2.80	44.84	46.0	52.36	60,600 80,700 70,650	4.20 3.50 3.85	660.0	Normal compression failure
						CONTROL (Oriented Fiber)						
35	Long L/D, Oriented fiber 5000-psi molding pressure	2.80	83.1	16.9	8.03	27.30	34.0	64.67	26,350†	2.74	446.0	Buckling failure
36	Same as above, except 100-psi molding pressure	2.07	57.8	42.2	6.37	59.86	66.0	33.7	64,200†	5.56	1001.0	Buckling failure
37	Same as above, except 1250-psi molding pressure	2.10	60.3	39.7	5.26	58.62	64.0	36.12	35,600†	6.12	1130.0	Buckling failure

* By difference.
** Control specimen, resin matrix only, no fiber, avg ult compressive strength 44,860 psi, and modulus 0.500 x 10^6 psi.
*** Avg of four specimens.
† Avg of two specimens.

NOTE: Resin matrix DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively.
Cure: 3 hr @ 200°F
        1 hr @ 300°F
        1 hr @ 400°F
Crocidolite asbestos mat: Amercoat C10-C15
Specimen configuration and test: ASTM D-695 (1/2 in. x 1/2 in. x 1 in.)

SECTION V

EVALUATION OF COMMERCIAL ORIENTED ASBESTOS REINFORCEMENT

Contact with Cape Insulation Ltd. in London revealed that one of their members had, at some time in the past, prepared oriented crocidolite felts, although there was no great demand for these materials. The material consisted of long crocidolite asbestos fibers laid parallel to each other and bonded with a thin veil of thermoplastic fibers, using a phenolic resin. They reported the following data (Table XXV), which created considerable interest:

TABLE XXV

CAPE INSULATION LTD. DATA FOR
PARALLEL-ORIENTED CROCIDOLITE FELTS INCORPORATING PHENOLIC RESIN

Processing	Orientation	Tensile Strength, psi	Flexural Strength, psi	Young's Modulus, $\times 10^6$ psi	Compressive Strength, psi	Shear Strength, psi
300°F molding temp	Parallel to reinforcement	58,000	15,300	6.5	25,000	6,000
1000-psi molding pressure						
10-minute molding time	At right angles to reinforcement	6,200	64,000	1.2	30,000	20,000
27 wt % laminate resin content						
1.85 sp gr						

From the work described in Section IV, we concluded that the specific gravity of 1.85 and resin content of 27.0% represented considerable void content in the British composites. It was believed that their good mechanical properties could be substantially improved if void content could be reduced. We decided to study the reinforcement further, particularly because it was a commercial material and would yield structural properties required in this research effort.

Raybestos-Manhattan, Inc., reported that they do not now have, nor does any market yet demand, an oriented asbestos fiber paper or mat. The Amercoat Corporation made a similar report. The Cape Insulation Ltd., people in Great Britian agreed to study Narmco's request for oriented crocidolite reinforcement.

A development order of Noramite crocidolite parallel-fiber asbestos rein-
forcement felt was received from Cape Insulation Ltd. The material consisted
of individual pieces of felt 9.5 x 9.5 in. and weighed 1.8 oz/ft^2. The con-
struction was actually a series of low-twist asbestos yarns side by side with
5% silica sol binder (see Figure 19). The material was used to fabricate a
4.5- x 1.75- x 0.625-in. high-pressure molding from solution-impregnated
epoxy. ASTM-D-695 compression specimens were used to evaluate the oriented
fiber composite and compare them with reinforcement stripped from crocidolite
ore. Table XXVI presents the results from this evaluation.
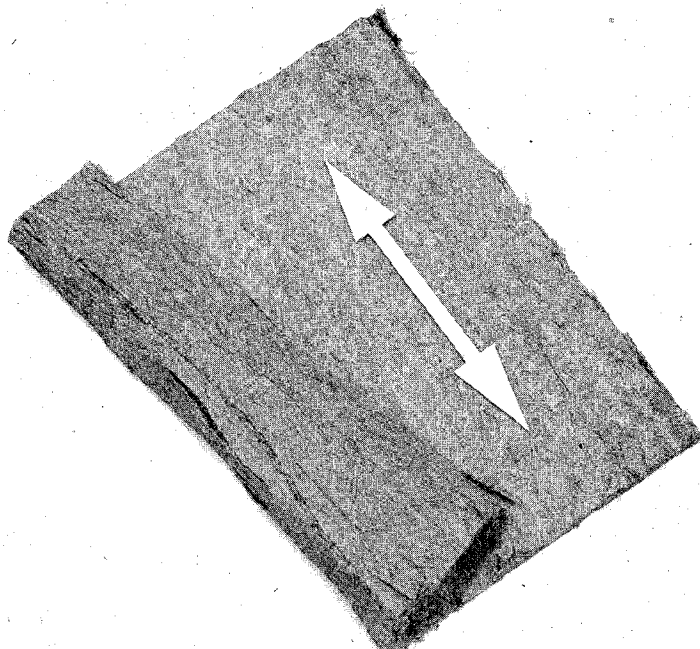
Figure 19. Noramite Crocidolite Parallel-Fiber
Asbestos Reinforcement Felt (Cape
Insulation, Ltd., London, England).
This specimen is 9.5 x 9.5 in. and
weighs 1.8 oz/ft^2. The construc-
tion is actually a series of low-
twist yarns, side by side, with
5% silica sol binder.

Solution impregnation with the epoxy resin was employed since it was con-
sidered to be the best procedure. Although the ultimate compressive strength
was not as good as with reinforcement stripped from crocidolite ore, a strength
of 53,600 psi was attained, with a modulus 1035.0% better than the resin matrix
and 16.2% better than the Amercoat C10-G15 random fiber crocidolite mat.

56

TABLE XXVI

COMPRESSION EVALUATION OF COMMERCIAL CROCIDOLITE PARALLEL-FIBER FELT
REINFORCED EPOXY MOLDING AT AMBIENT TEMPERATURE

Speci-men No.	Processing	Sp Gr	Wt % Asbestos Fiber*	Wt % Resin Matrix	Vol % Void (Calc)	Vol % Resin Difference	Vol % Resin Charted	Vol % Asbestos (Calc)	Ult Compressive Strength, psi	Compressive Modulus psi×10^6	Improvement in Modulus** %	Comments
						SOLUTION IMPREGNATIONS (Specimen Ends Reinforced)						
39	Control, Long L/D Oriented fiber*** 1250-psi molding pressure	2.36	72.6	27.4	3.60	46.74	50.0	49.66	112,200 <u>92,900</u> 102,600	8.23 <u>2.17</u> 5.20	938.0	Normal compression failure
46	Commercial Felt, Long L/D, Oriented fiber,† 4,000 molding pressure	2.29	72.4	27.6	0.75	50.59	49.0	49.41	46,100 53,700 61,000 61,000 52,500 54,900 53,500 <u>46,100</u> 53,600	5.90 5.53 5.66 5.66 5.78 5.29 5.90 <u>5.66</u> 5.67	1035.0	Buckle or delamination failure back of reinforced ends
						SOLUTION IMPREGNATIONS (Specimen Ends Nonreinforced)						
31	Control, Long L/D, random fiber‡ 5000 psi molding pressure	2.38	75.3	24.7	1.21	45.63	46.0	53.16	35,400 36,300 37,200 <u>36,300</u> 36,300	5.16 4.57 4.62 <u>5.17</u> 4.88	876.0	Shatter type failure

* By difference.

** Control specimen, resin matrix only, no fiber, avg ult compressive strength 44,860 psi, and modulus 0.500 × 10^6 psi.

*** Fiber stripped from ore and opened into array with pressure rolls.

† Noramite, Cape Insulation Ltd., London, England.

‡ Amercoat C10-G15 mat.

NOTE: Resin matrix DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively.
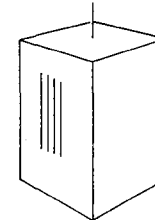Cure: 3 hr @ 200°F
      1 hr @ 300°F
      1 hr @ 400°F
Specimen configuration and test: ASTM D-695 (1/2 in. x 1/2 in. x 1 in.)

Fiber Orientation
1.75 in. x 4.5 in. x 5/8 in.
Unidirectional Molding

Four 6- x 6- x 1/8-in. unidirectional crocidolite flat panels were also made for a comprehensive flexure, tension and compression evaluation (Federal Test Method Standard No. 406) of the reinforcement at room temperature and 0°, 45°, and 90° fiber orientation. Bulk epoxy resin properties were generated in order to supply a complete profile of the reinforcement potential of the parallel asbestos felt.

Tables XXVII, XXVIII and XXIX present tension, flexure, and compression properties, respectively. Figure 20 shows that the laminate specimens had close to zero void and represent the best attempt at optimum composite composition. Figures 21, 22, and 23 are polar plots (0°, 45°, and 90° fiber orientation) of tensile, flexural, and compressive ultimate strength and modulus.

Ultimate tensile strength was 58,000 psi with a 8.76×10^6 psi modulus (0°). The 45° properties were almost comparable with the random fiber mat, and the 90° properties were almost identical with the nonreinforcement bulk resin control, as expected.

Ultimate flexural strength was 91,000 psi with a 9.13×10^6 psi modulus (0°). The 45° properties were roughly 50% of the random fiber mat, and once again the 90° properties were almost identical with the bulk resin control.

Ultimate compressive strength was 63,775 psi with a 8.62×10^6 modulus (0°). The 45° properties were almost identical with the random fiber mat properties, and 90° properties were close to bulk resin control properties.

The investigation was considered very rewarding. The properties reported for the reinforcement with a phenolic resin were exceeded, using a lower strength epoxy resin.

TABLE XXVII

TENSILE STRENGTH AND MODULUS EVALUATION OF
COMMERCIAL CROCIDOLITE PARALLEL-FIBER FELT REINFORCEMENT OF
EPOXY FLAT PANELS* AT AMBIENT TEMPERATURE

Speci-men No.	Processing	Sp Gr	Wt % Asbestos Fiber**	Wt % Resin Matrix	Vol % Void (Calc)	Vol % Resin Difference	Vol % Resin Charted	Vol % Asbestos (Calc)	Ult Tensile Strength, psi	Tensile Modulus, psix10^6	Improvement in Modulus, %	Comments
						CONTROL, BULK RESIN, NO REINFORCEMENT						
	No pressure casting	1.24	0	100	0	100	100	0	8,000 6,500 4,100 6,100 7,500 6,400	0.51 0.45 0.42 0.42 0.56 0.47	0	Normal tensile failure
						FIBER*** ORIENTED 0°						
49-1 49-2 49-3 49-4 49-5	3000-psi molding pressure, solution impregnation	2.27	71.8	28.2	0.56	50.77	50.0	48.67	54,500 57,000 59,000 58,000 61,300 58,000	10.39 8.14 8.31 8.88 8.10 8.76	1770.0	Some initial failure in crips, re-broken
						FIBER ORIENTED 45°						
47-1 47-2 47-3 47-4	3000-psi molding pressure, solution impregnation	2.27	77.6	22.4	6.10	37.56	44.0	56.34	-- 17,700 15,800 16,200 16,600	-- 3.78 4.65 3.91 4.11	775.0	Normal tensile failure
						FIBER ORIENTED 90°						
48-1 48-2 48-3 48-4 48-5	3000-psi molding pressure, solution impregnation	2.26	74.1	25.9	2.52	45.89	49.0	51.59	7,500 7,100 7,300 7,700 9,500 7,820	3.24 3.12 2.34 2.11 2.48 2.66	465.0	Normal tensile failure
						CONTROL, NONORIENTED AMERCOAT C10-G15 MAT						
	3000-psi molding pressure, solution impregnation	2.19	66.3	33.7	3.11	45.40	57.0	42.29	22,000 28,000 31,900 36,100 29,500	4.72 3.71 4.39 4.31 4.28	814.0	Normal tensile failure

* 6 x 6 x 1/8-in. unidirectional panel.

** By difference.

*** Normite, Cape Insulation Ltd., London, England. See Appendix B for tensile specimen design.

NOTE: Resin matrix DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively
Cure: 3 hr @ 200°F
      1 hr @ 300°F
      1 hr @ 400°F
Specimen configuration and test: 1/2 x 6 x 1/8 in. with end doublers.

TABLE XXVIII

FLEXURAL STRENGTH AND MODULUS EVALUATION OF COMMERCIAL CROCIDOLITE PARALLEL-FIBER FELT REINFORCEMENT OF EPOXY FLAT PANELS* AT AMBIENT TEMPERATURE

Specimen No.	Processing	Sp Gr	Wt % Asbestos Fiber**	Wt % Resin Matrix	Vol % Void (Calc)	Vol % Resin Difference	Vol % Resin Charted	Vol % Asbestos (Calc)	Ult Flexural Strength, psi	Flexural Modulus, psix10⁶	Improvement in Modulus, %	Comments
CONTROL, BULK RESIN, NO REINFORCEMENT												
	No pressure, casting	1.24	0	100	0	100	100	0	16,700 / 14,000 / 20,400 / 22,200 / 16,200 / 17,900	0.60 / 0.58 / 0.59 / 0.57 / 0.57 / 0.58	0	Normal flexural failure, failing in tension on tension side
FIBER*** ORIENTED 0°												
49-1 / 49-2 / 49-3 / 49-4 / 49-5	3000-psi molding pressure, solution impregnation	2.27	71.8	28.2	0.56	50.77	50.0	48.67	96,800 / 87,100 / 86,700 / 95,100 / 89,300 / 91,000	9.04 / 9.16 / 8.95 / 9.18 / 9.30 / 9.13	1480.0	Normal flexural failure, failing in tension on tension side
FIBER ORIENTED 45°												
47-1 / 47-2 / 47-3 / 47-4 / 47-5	3000-psi molding pressure, solution impregnation	2.27	77.6	22.4	6.10	37.56	44.0	56.34	36,900 / 29,400 / 36,300 / 26,100 / 32,200	4.55 / 3.92 / 4.40 / 3.66 / 4.13	612.0	Normal flexural failure, failing in tension on tension side
FIBER ORIENTED 90°												
51-1 / 51-2 / 51-3 / 51-4 / 51-5	3000-psi molding pressure, solution impregnation	2.28	73.6	26.4	1.08	47.98	50.0	50.94	20,800 / 22,000 / 21,200 / 18,300 / 18,700 / 20,200	3.00 / 2.90 / 2.77 / 2.84 / 2.83 / 2.86	394.0	Normal flexural failure, failing in tension on tension side
CONTROL, NONORIENTED AMERCOAT C10-G15 MAT												
	3000-psi molding pressure, solution impregnation	2.19	66.3	33.7	3.11	45.40	57.0	42.29	65,100 / 60,000 / 61,700 / 62,300	4.60 / 3.89 / 4.30 / 4.26	635.0	Normal flexural failure, failing in tension on tension side

* 6 x 6 x 1/8-in. unidirectional panel.

** By difference.

*** Noramite, Cape Insulation Ltd., London, England.

NOTE: Resin matrix DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively.
    Cure: 3 hr @ 200°F
          1 hr @ 300°F
          1 hr @ 400°F
    Specimen configuration and test: 1/2 x 4 x 1/8-in. Federal Test Method Standard No. 406, Method 1031 (Narmco ETM 201).

TABLE XXIX

COMPRESSIVE STRENGTH AND MODULUS EVALUATION OF COMMERCIAL CROCIDOLITE PARALLEL-FIBER FELT REINFORCEMENT OF EPOXY FLAT PANELS* AT AMBIENT TEMPERATURE

Specimen No.	Processing	Sp Gr	Wt % Asbestos Fiber**	Wt % Resin Matrix	Vol % Void (Calc)	Vol % Resin Difference	Vol % Resin Charted	Vol % Asbestos (Calc)	Ult Compressive Strength, psi	Compressive Modulus, psi×10⁶	Improvement in Modulus, %	Comments
						CONTROL, BULK RESIN, NO REINFORCEMENT						
	No pressure, casting	1.24	0	100	0	100	100	0	22,100 / 22,000 / 21,500 / 21,800 / 18,800 / 21,200	0.54 / 0.54 / 0.54 / 0.55 / 0.54 / 0.54	0	Shatter type failure
						FIBER** ORIENTED 0°						
51-1 / 51-2 / 51-3 / 48-4 / 48-5	3000-psi, molding pressure	2.28 ... 2.26	73.6 ... 74.1	26.4 ... 25.9	1.08 ... 2.52	47.98 ... 45.89	50.0 ... 49.0	50.94 ... 51.59	68,800 / 66,300 / -- / 54,800 / 65,200 / 63,775	9.06 / 9.13 / -- / 9.63 / 6.66 / 8.62	1500.0	Normal compression failure
						FIBER ORIENTED 45°						
47-1 / 47-2 / 51-3 / 51-4	3000-psi, molding pressure	2.27 ... 2.28	77.6 ... 73.6	22.4 ... 26.4	6.10 ... 1.08	37.56 ... 47.98	44.0 ... 50.0	56.34 ... 50.94	36,900 / 30,200 / 45,400 / 47,600 / 40,025	4.22 / 4.35 / 4.21 / 4.04 / 4.20	680.0	Normal compression failure
						FIBER ORIENTED 90°						
49-1 / 49-2 / 48-3 / 48-4 / 48-5	3000-psi, molding pressure	2.27 ... 2.26	71.8 ... 74.1	28.2 ... 25.9	0.56 ... 2.52	50.77 ... 45.89	50.0 ... 49.0	48.67 ... 51.59	36,000 / 33,100 / 35,900 / 18,000 / 14,800 / 28,725	2.93 / 3.03 / 2.84 / 2.59 / 2.58 / 2.82	422.0	Normal compression failure
						CONTROL, NONORIENTED AMERCOAT C10-G15 MAT						
	3000-psi, molding pressure	2.19	66.3	33.7	3.11	45.40	57.0	42.29	36,400 / 44,300 / 40,000 / 41,200 / 40,500	4.39 / 4.97 / 4.21 / 4.45 / 4.50	732.0	

* 6 x 6 x 1/8-in. unidirectional panel.

** By difference.

*** Noramite, Cape Insulation Ltd., London, England.

NOTE: Resin matrix DEN 438/MNA/DMP-30; 100/101/0.75-pbw, respectively.
 Cure: 3 hr @ 200°F
  1 hr @ 300°F
  1 hr @ 400°F
 Specimen configuration and test: 1 x 3 x 1/8-in. ATC Report No. ARTC-11, Method No. I (Narmco ETM 301).
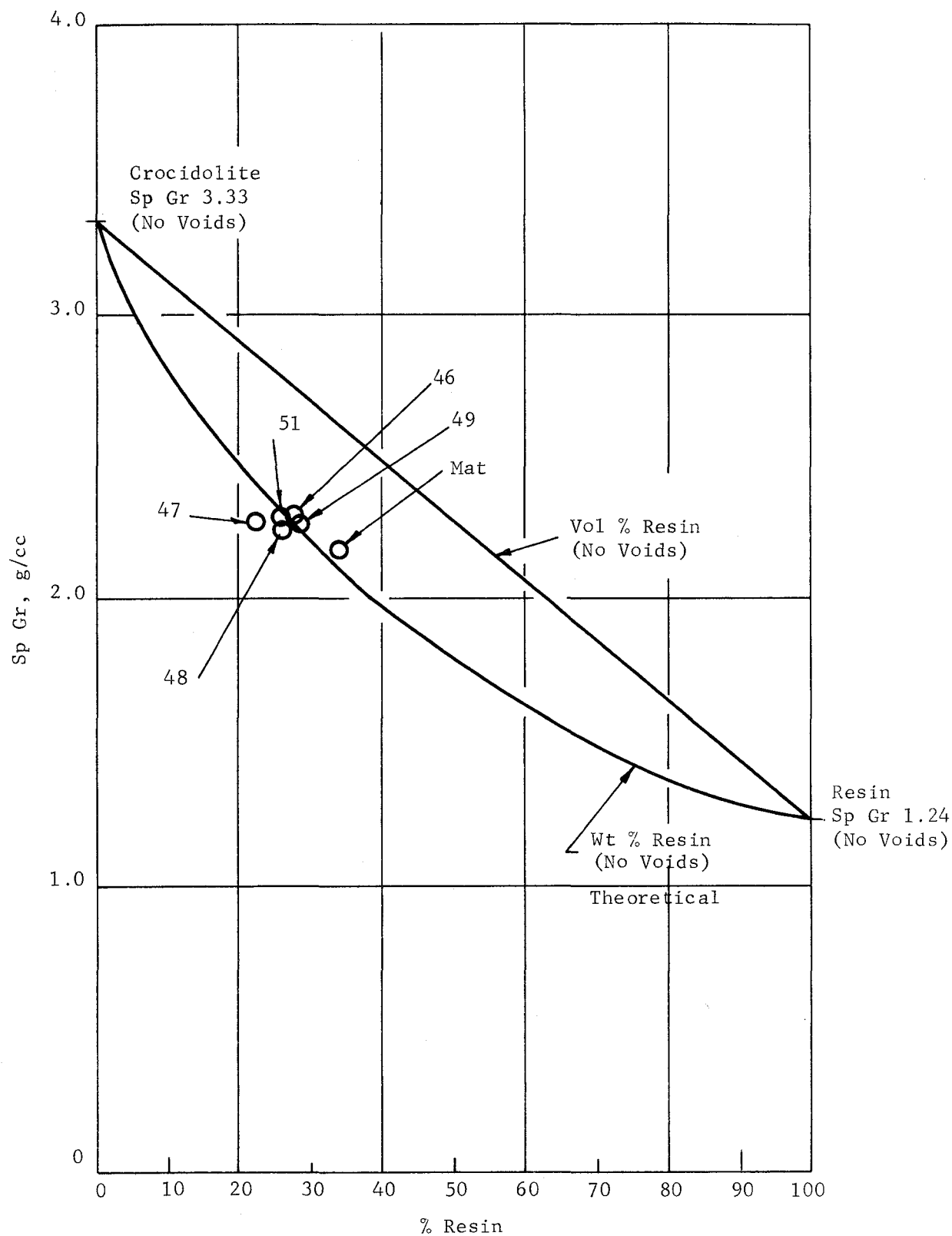
61

Figure 20. Specific Gravity and Resin Weight and
Volume Percentages for Unidirectional
Crocidolite Epoxy Composites Indicating
Extremely Low Void Contents. The
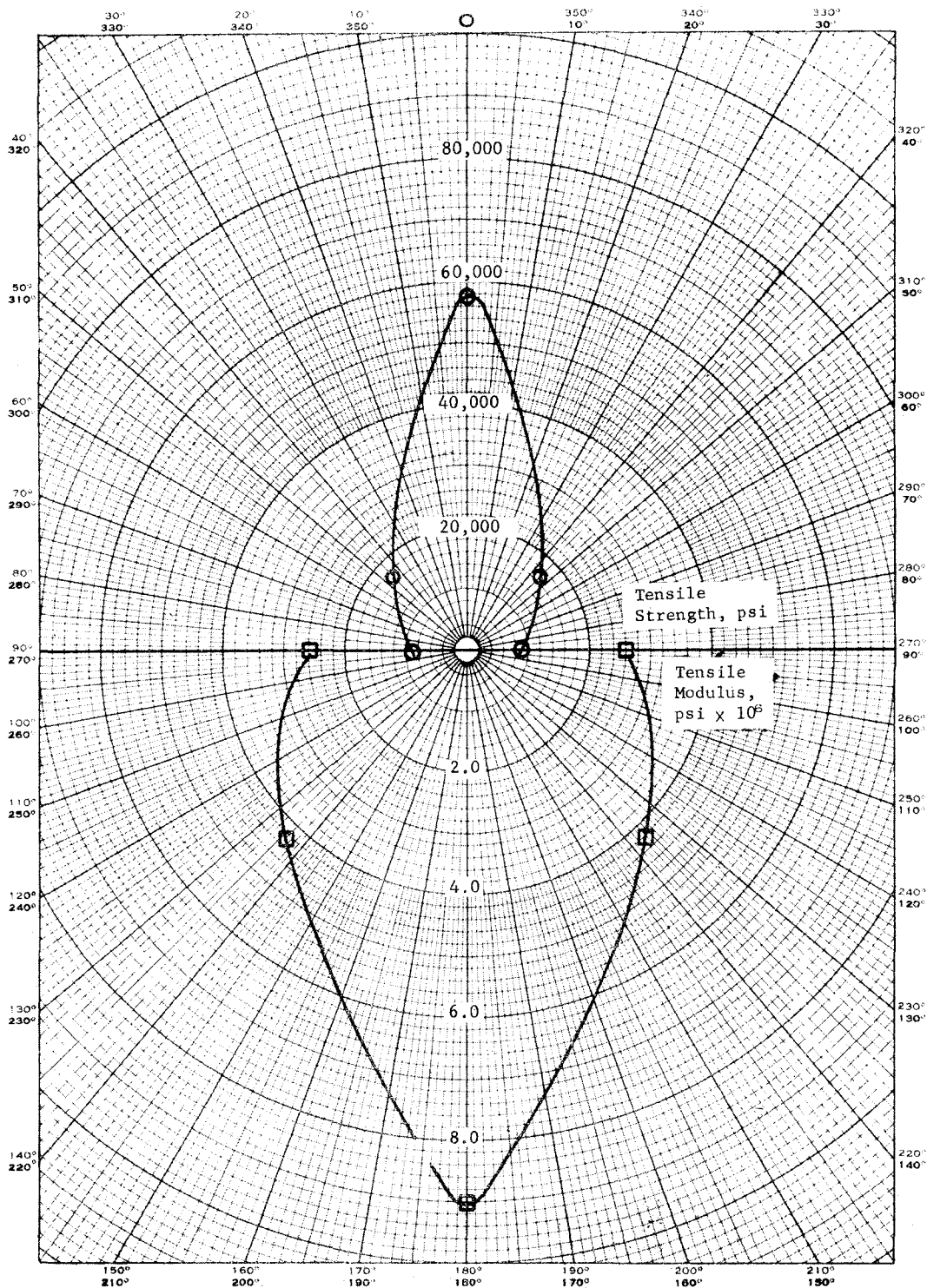plotted points represent weight per-
cent resin.

Figure 21. Polar Plot of Tensile Strength and Modulus for
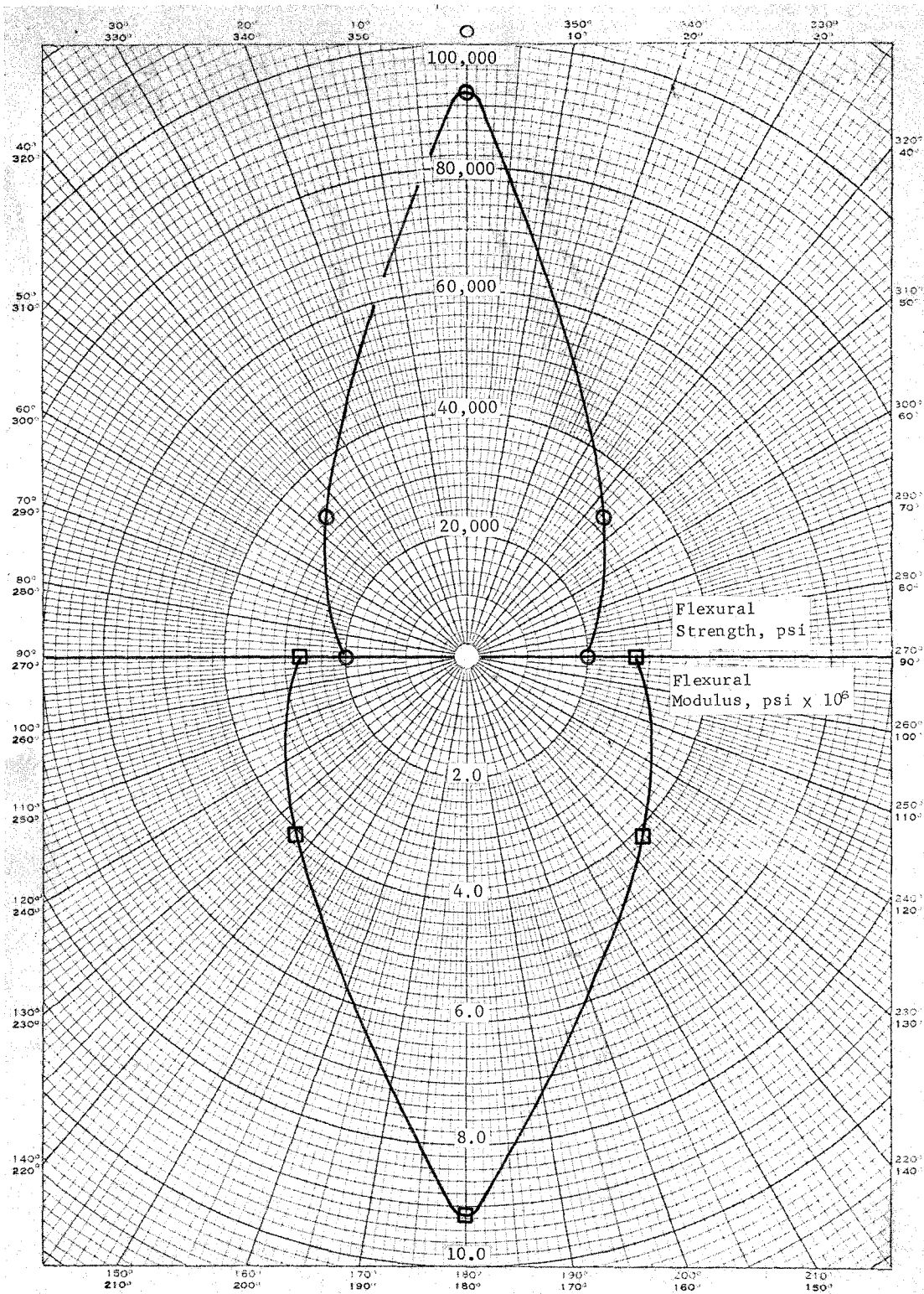Unidirectional Crocidolite Epoxy Flat Laminates

63

Figure 22. Polar Plot of Flexural Strength and Modulus for
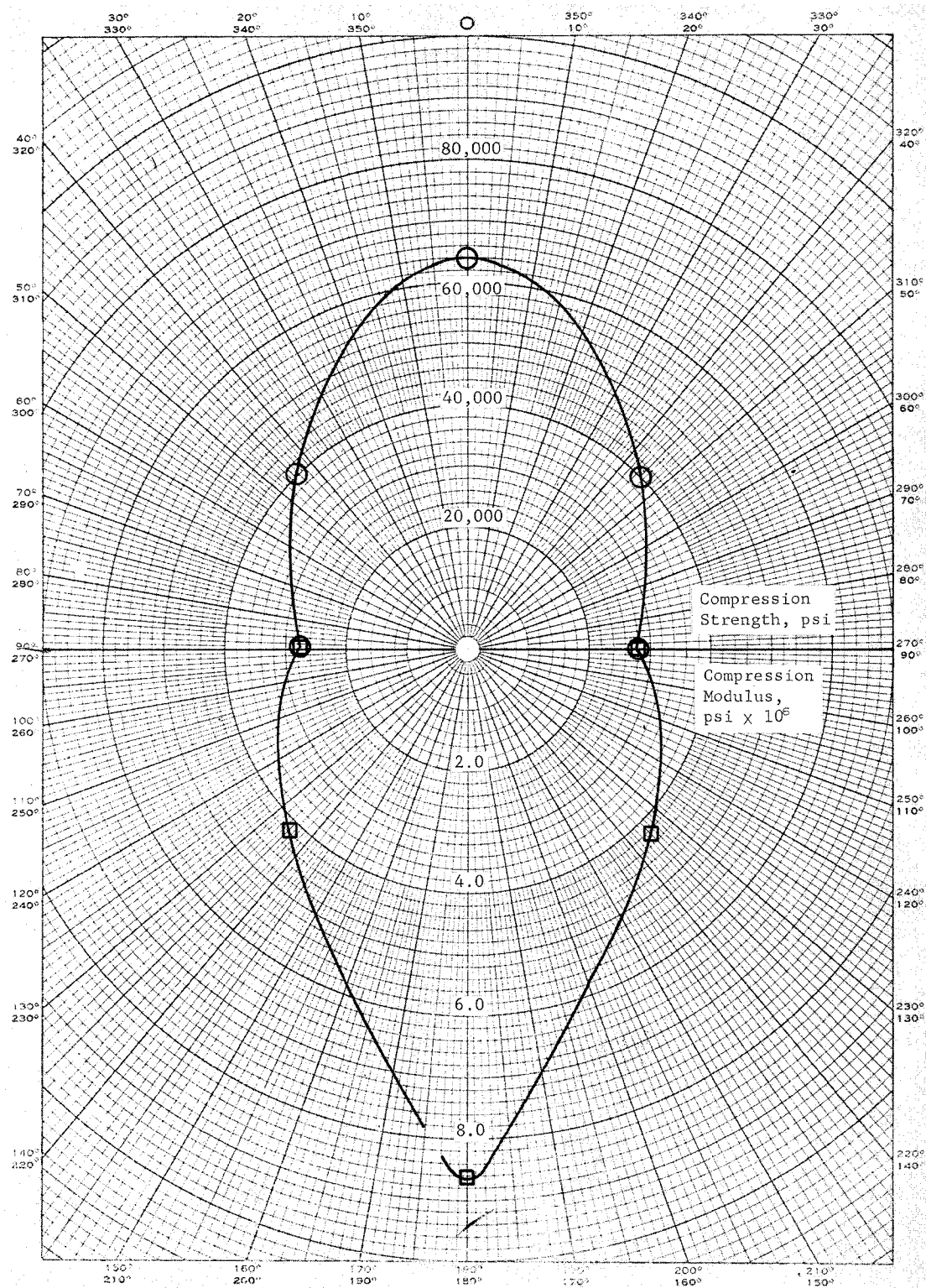Unidirectional Crocidolite Epoxy Flat Laminates

Figure 23. Polar Plot of Compression Strength and Modulus for
Unidirectional Crocidolite Epoxy Flat Laminates

SECTION VI

EVALUATION OF POLYIMIDE LAMINATES WITH
ORIENTED ASBESTOS REINFORCEMENT

Because of the excellent properties obtained with the commercial parallel
fiber crocidolite and epoxy resin, we decided to use the small remaining scraps
of the development order of oriented fiber felt and impregnate them with Sky-
bond 700 polyimide resin to note any upgrading in mechanical properties that
might be attained. High pressure and what was considered to be optimum resin
content and specific gravity were obtained for four laminates (Nos. 53, 54,
55 and 56). Figure 24 shows that these laminates had very low void content,
the closest yet to theoretical. Respective flexural strength and modulus
values were 41,500 psi and 5.79 $\times$ 10^6 psi prior to postcure and after a cure
of 600°F.

When the laminates were postcured in exactly the same manner as were the
earlier, random polyimide laminates, the last stage of the 4-hour exposure to
700°F in air left the laminates almost completely burned out. There was
hardly sufficient resin to hold the mass of fibers together.

It was reasoned that the parallel fibers were allowing a "channel oxida-
tion" of the resin parallel with the fibers. It was further conjectured that
there may be a chemical reaction between asbestos and polyimide at elevated
temperature which degrades the system. In any event, an inert atmosphere
cure and postcure appeared to be required to bring the polymer to full state
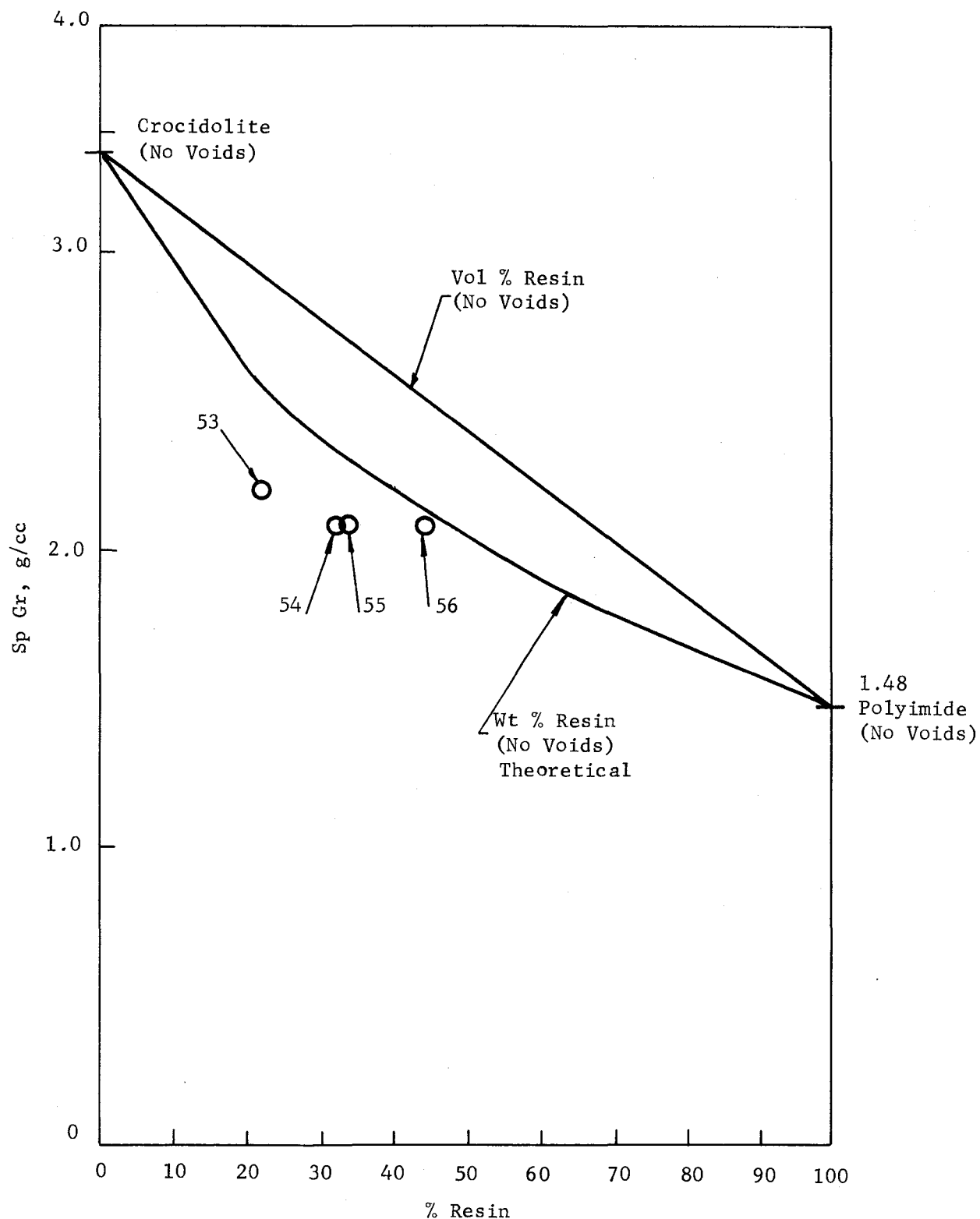of cure prior to exposure of the composite to an oxidizing medium.

Figure 24. Specific Gravity and Resin Weight and Volume Percentages for Skybond 700 Polyimide Laminates of Parallel Fiber Crocidolite Reinforcement, Showing the Comparatively Lower Voids than Previous Polyimide Efforts. The plotted points represent weight percent resin.

SECTION VII

SUMMARY

In retrospect, the studies conducted during this program would appear to underscore the potential of materials made from high-temperature polymers combined with asbestos fiber reinforcement.

While work with a crocidolite asbestos mat/polyimide resin laminate (the initial candidate for process optimization studies) failed to yield respectable flexural strengths, it did point out two problem areas which helped to define the course future work would take: that of inadequate wetting of the asbestos fibers, and the excessive volatiles now inherent in existing polyimide systems. The fundamental asbestos studies initiated to improve wetting of the asbestos fibers pointed out that these fibers are very sensitive to buckling, and that voids in the resin matrix cannot be tolerated. Work was thus centered on the use of epoxy resin which, being 100% solids, does not develop volatiles and the resultant voids. Potting of crocidolite ore in an epoxy resin matrix and subsequent compression testing of the composite yielded a fiber modulus of 43 million psi, thus establishing the potential of the reinforcement.

The numerous fiber classification, orientation, wetting, and surface studies undertaken resulted in processing conditions which may be considered optimum for the composite investigated. Dilute methyl ethyl ketone solutions of epoxy resin provide the best fiber impregnation. Resin content is optimum at approximately 25 weight percent and specific gravity at 2.4 g/cc. Because of the sensitivity of the fiber to buckling, percentage of voids in the composite must be held under 1.5 volume percent. The optimum processing pressure for crocidolite and epoxy composites is between 1000 and 5000 psi, and oriented rather than random fiber provides the best results.

Recommended for future investigations into improved polymer or binder systems for asbestos fibers are some of the more refined polyimides; the polybenzimidazoles, both aliphatic and aromatic; the unique binders which react chemically with the asbestos fiber; the high conversion silicones; and the inorganic types that are now emerging. Particularly exciting is the potential offered by the ecomonical chrysotile and crocidolite asbestos (as low as $1.00 per pound) when viewed in light of the superior reinforcement properties which this program has shown to be attainable.

MATERIALS IDENTIFICATION

Material Designation	Supplier
Blue Crocidolite Paper	W. M. Schulz Company Irwindale, California
C10-G15 Crocidolite Asbestos Mat	Amercoat Corporation Ardmore, Oklahoma
Curing Agent Z	Shell Chemical Company
Epon 815	Shell Chemical Company
FreKote 33 Parting Agent	Frekote, Inc. Boca Raton, Florida
Novabestos 7301	Raybestos-Manhattan Bridgeport, Connecticut
Novabestos 7311	Raybestos-Manhattan Bridgeport, Connecticut
Paper "A"	Johns-Manville Manville, New Jersey
Paper "F"	Johns-Manville Manville, New Jersey
8122 Polyimide Resin*	DuPont
Pyrotex 40 RPD	Raybestos-Manhattan Bridgeport, Connecticut
Pyrotex 70 RPD	Raybestos-Manhattan Bridgeport, Connecticut
Skybond 700	Monsanto Springfield, Massachusetts
Skybond 701	Monsanto Springfield, Massachusetts
Style 116 Glass Fabric	J. P. Stevens & Company, Inc. New York, New York
Style 1500 Glass Fabric	J. P. Stevens & Company, Inc. New York, New York
TFE-30 Teflon Dispersion	E. I. du Pont de Nemours & Co., Inc. Wilmington, Delaware

* Discontinued.

NOTE: Barrier material: 116 Style glass fabric coated with TFE-30 Teflon dispersion, sintered at $800°-810°F$. Total resin pickup $30\%\pm2\%$.

Material	Supplier
Crocidolite Fiber	Amercoat Corporation, Ardmore, Oklahoma
Crocidolite Ore Specimens	Cape Insulation Limited, London, England, and North American Asbestos Corporation, Chicago, Illinois
DEN-438 Epoxy Novolac Resin	The Dow Chemical Company, Midland, Michigan
Methyl Nadic Anhydride	E. V. Roberts and Associates, Incorporated, Culver City, California
DMP-30	E. V. Roberts and Associates, Incorporated, Culver City, California
Asbestos Fiber Filaments	New Products Department Carborundum Company, Niagara Falls, New York
Skybond 700 and 701	Monsanto, Springfield, Massachusetts
Noramite Parallel Fiber Crocidolite Felt	Cape Insulation Ltd., London, England
Barrier	Prepared in the Laboratory. Two plies style 116 glass fabric integrally coated with DuPont TFE #30 fluorocarbon resin dispersion (60%±5% solids). Sintered 5 minutes at 800°-810°F. Acceptable resin content 30%±2% by weight. Used adjacent to prepreg.
Breather	Two plies style 1500 style glass fabric Used away from prepreg and adjacent to barrier.

Equipment	Supplier
Vibro-Fluidizer, Model B	Armstrong Products Company, Warsaw, Indiana
Ultrasonic Generator and Tank, Model UG-140, Serial 20044, 54.0 Kilocycle Output	Ultrasonics Corporation, Los Angeles California

70

CALCULATIONS AND TEST METHOD STANDARDS

$$\% \text{ Resin Pickup} = \frac{\text{Prepreg Wt} - \text{Asbestos Wt}}{\text{Prepreg Wt}} \times 100$$

(10 plies 9 in. x 9 in.)

$$\% \text{ Volatiles} = \frac{\text{Prepreg Original Wt} - \begin{array}{c}\text{Prepreg Wt after}\\ \text{10 min @ 430°F}\end{array}}{\text{Prepreg Original Wt}} \times 100$$

(Single ply 4 in. x 4 in.)

$$\% \text{ Flow} = \frac{\text{Prepreg Original Wt} - \text{Deflashed Laminate Wt}}{\text{Prepreg Original Wt}} \times 100$$

(10 plies 9 in. x 9 in.)

$$\% \text{ Calc. Resin} = \frac{\text{Deflashed Laminate Wt} - \text{Asbestos Wt}}{\text{Deflashed Laminate Wt}} \times 100$$

(10 plies 9 in. x 9 in.)

$$\text{Sp Gr} = \frac{\text{Deflashed Laminate Wt}}{\begin{array}{c}\text{Deflashed Laminate}\\ \text{Wt in Air}\end{array} - \begin{array}{c}\text{Deflashed Laminate}\\ \text{Wt in Water}\end{array}}$$

(Federal Test Method Standard No. 406, Method 5011)

$$\% \text{ Laminate Void} = V_v = 1 - \frac{w_c}{w_r}\left[1 + \left(\frac{w_r}{w_m} - 1\right) M_w\right] \times 100$$

where

V_v is the void content volume fraction

M_w is the matrix content weight fraction (measured)

w_c is the composite density (measured)

w_r is the reinforcement density (known)

w_m is the matrix density (known)

Flexural Properties

Per Narmco Research & Development Division Engineering Test Method No. 201 (Federal Test Method Standard No. 406, Method 1031; ASTM D-790; and ATC Report No. ARTC-11, Method VIII.)

Heat Aging

Heat aging at 600°F conducted in an air-circulating oven on flexural specimens conforming with Federal Test Method Standard No. 406. Specimens wrapped in 181 glass fabric, and subsequently in 5-mil aluminum foil to prevent direct contact with oven air stream.

Compression Properties

1. Per Narmco Research & Development Division Engineering Test Method No. 201 (ATC Report No. ARTC-11, Method No. 1).

2. Per ASTM-D-695.

Tensile Properties

Per accompanying specimen design to conserve material.

Tensile Specimen (Unidirectional Asbestos Fibers)
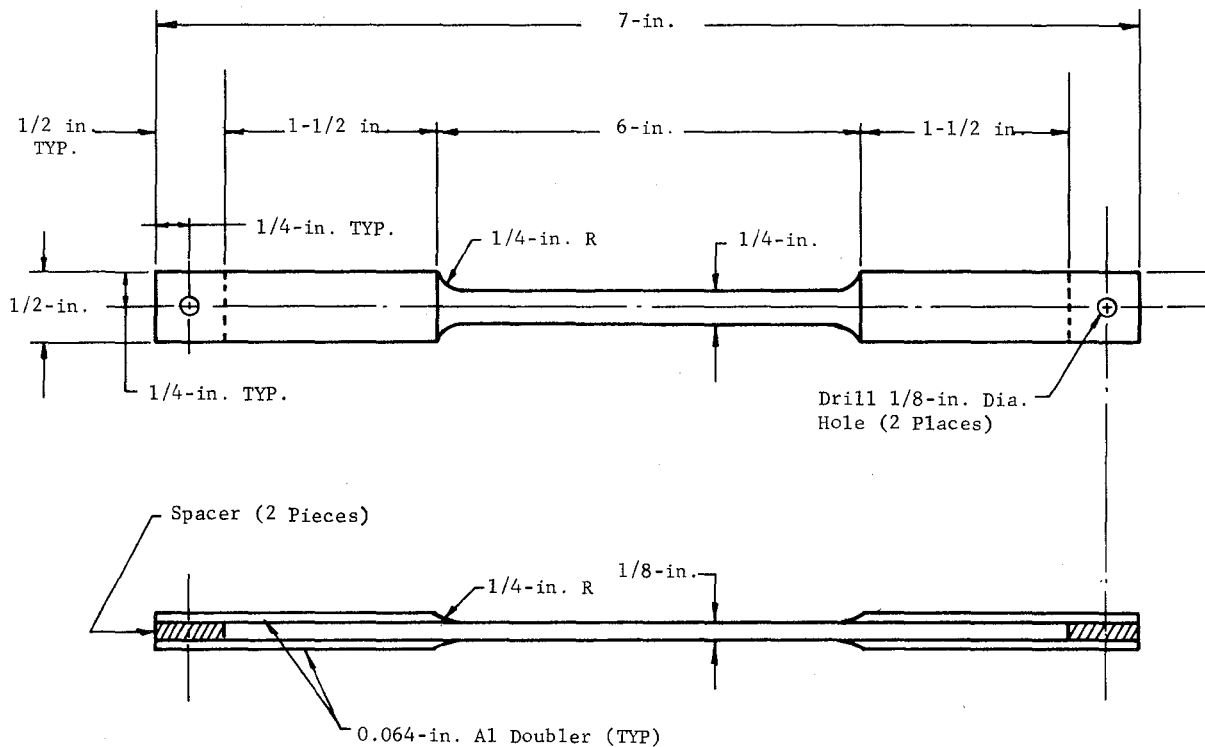
NOTE: Doublers and spacers bonded with M329 after machining.

Percent Resin (Moldings):   3 hours at 1050°F

Specific Gravity (Moldings):   Federal Test Method Standard No. 406, Method 5011

Percent Void (Moldings):

$$V_v = 1 - \frac{w_c}{w_r}\left[1 + \left(\frac{w_r}{w_m} - 1\right)M_w\right] \times 100$$

where

V_v is the void content volume fraction

M_w is the matrix content weight fraction (measured)

w_c is the composite density (measured)

w_r is the reinforcement density (known)

w_m is the matrix density (known)

Compression Properties: Per ASTM D-695

BIBLIOGRAPHY

Anonymous, "Asbestos as a Reinforcement," Reinforced Plastics, 22-25 (September-October 1965)

Anonymous, Asbestos, Phenolic Resin Impregnated, Low Pressure Laminating, Final Specification No. AGC-44043, Aerojet-General Corporation, Sacramento, California, 18 September 1964, AD-465 654

Anonymous, Bibliography on Reinforced Plastics, Report No. MAC-LB-425-4, AD-816 818L, McDonnell Aircraft Corporation, St. Louis, Missouri, January 1967

Anonymous, Handbook of Asbestos Textiles, Asbestos Textile, Schoolhouse Lane, Philadelphia 44, Pennsylvania

Anonymous, Resinated Asbestos Materials, Report No. 5 of Subcommittee 70, AD-489-235, Joint Airworthiness Committee, Great Britain, May 1966

Asbestos, Phenolic Resin Impregnated, Low Pressure Laminating, Final Specification, AD-465 654, Aerojet-General Corporation, Sacramento, California, 18 September 1964

Badollet, M. S., "Asbestos, A Mineral of Unparalleled Properties," Can. Inst. Min. Met., 54, 151-160 (1951)

Badollet, M. S., "Asbestos Reinforcements," Modern Plastics Encyclopedia, 1962

Barrable, V. E., Alexander Bennett, and A. F. Jerome, "Use of Crocidolite Asbestos in Reinforced Plastics" (paper presented to the 18th Annual Conference of the Society of the Plastics Industry, Reinforced Plastics Division, Chicago, Illinois, February 1963); see also Industrial Chemistry, 2, 186-189 (September 1963)

Berg, K. N., "Crocidolite Asbestos Reinforcement; Current Information on Crocidolite," Narmco Internal Report No. ATS 225-031, Narmco Research & Development, San Diego, California, 7 July 1967

Berger, Hans, Asbestos Fundamentals, Chemical Publishing Company, 212 Fifth Avenue, New York, 1963

Berger, Hans, Asbestos with Plastics and Rubber, Chemical Publishing Company, Tudor, 1966

Boller, Kenneth H., "Fatigue Characteristics of Reinforced Plastic Laminates Subjected to Axial Loading," Modern Plastics, 41 (10), 145-146, 148, 150, 188 (1964)

Boller, Kenneth H. and Kenneth E. Kimball, Effect of Elevated Temperatures on Weight Loss and Flexural Properties of Three Reinforced Plastic Laminates, WADC TR 59-216, AD-232 962, Contract AF 33(616)58-1, US Department of Agriculture, Forest Products Laboratory, Madison, Wisconsin, February 1959

Boller, Kenneth H., Strength Properties of Reinforced Plastic Laminates at Elevated Temperatures (Silicone-Asbestos, R/M Pyrotex Felt 45-RPD), ASD TDR 62-406, AD 289-066, Contract AF 33(616)61-06, US Department of Agriculture, Forest Products Laboratory, Madison, Wisconsin, September 1962

Brown, Carolyn E., A Study of the Hydrothermal Synthesis of Chrysotile Asbestos, Mechanical Engineering Report No. MS-112, AD-473 729, National Aeronautical Establishment, Ottowa, Ontario, December 1964

Carroll-Purczynski, C. Z., "Asbestos in Composite Materials," Engineering Materials and Design, Part I: 31-33 (January 1962); Part II: 98-102 (February 1962)

Carroll-Purczynski, C. Z., Asbestos from Rock to Fabric, Textile Institute, Manchester, England, 1956

Cornwell, A. C., Evaluation of Two Asbestos-Reinforced Plastic Materials, Technical Note No. Chem 1367, AD 264 014, Royal Aircraft Establishment, Great Britain, December 1960

Crawley, William P., "Heat-Resistant Fibrous Products Containing Ceramic Fibers" (to Carborundum Company), US Patent 3,090,103, 21 May 1963

Crouch, R. T. and J. J. Thomas, "Asbestos Reinforcement in Premix Molding Compounds," Reinforced Plastics (July-August 1966)

Cryor, Robert E., "Asbestos-Reinforced Plastic Pipe," Chemical Engineering (2 August 1965)

Cryor, Robert E., "Asbestos Reinforced Plastics Resist Heat and Chemicals," Materials in Design Engineering (April 1966)

Davidson, Theodore and Bernhard Wunderlich, Comparison of Extended Polyethylene and Chrysotile Asbestos Fracture Surfaces, Technical Report No. 7, AD-609 608, Contract NOnr 59119, Rensselaer Polytechnic Institute, Troy, New York, 15 October 1964

Davis, Thomas R. Jr., Investigation of the Elevated Temperature Characteristics of Plastic Laminates, Final Report, AD-477 593, Naval Engineering Center, Aeronautical Materials Laboratory, Philadelphia, Pennsylvania, January 1966

Denney, M. A. and J. C. Martingdale, "Plastics in Aircraft. IV. Testing of Reinforced Plastics at Elevated Temperatures," Aircraft Engineering, 35, 10-13 (1963); see also International Aerospace Abstracts, 3 (6), Abstract No. A63-12600 (1963)

Doyle, Harry J., Development of Design Data for the Application of Phenolic Asbestos Laminates on Fire Vehicle Heat Protective Systems. Addendum: Ablation Resistance of Phenolic Asbestos Laminate, Document N62-19300, NASA CR-50827, Republic Aviation Corporation, Farmingdale, New York, 18 June 1963; see also Sci. Tech. Aerospace Report, 1 (18), 1410 (1963)

Farmer, R. W., "Isothermal Thermogravimetry of Reinforced Plastics," Proceedings of the Annual Technical Management Conference of the Society of the Plastics Industry, Reinforced Plastics Division, Vol. 19 (4-G), 12 pp (1964)

Flom, Donald G. et al., High-Strength, High-Modulus, Whisker Reinforced Plastic Composites, AFML TR-66-362, AD-817 953L, Contract AF 33(615)-2997, General Electric Company, Missile and Space Division, Philadelphia, Pennsylvania, February 1967

Frazier, S. E. et al., <u>An Inherently Fibrous Polymer</u>, Contribution from the Departments of Chemistry & Geology, Case Western Reserve University, Cleveland, Ohio, 44106, <u>Inorganic Chemistry</u>, Vol. 6, No. 9, September 1967

Heywood, R. B., <u>Present and Potential Fatigue and Creep Strengths of Reinforced Plastics</u>, RAE-TN-Chem 1337, Document N65-20632, Royal Aircraft Establishment, Farmborough, England, October 1958

Hodgson, A. A., "Fibrous Silicates," Lecture Series, Cape Asbestos Fibres Limited, 114 and 116 Park Street, London W-1, England

Howse, Paul T. Jr., and C. D. Pears, "Thermal Properties of Reinforced Plastics," <u>Modern Plastics</u>, <u>39</u> (1), 140, 142-144, 146, 149, 153, 246, 248 (1961)

Jenkins, G. F., "Asbestos," <u>Industrial Minerals and Rocks</u>

Juhl, D. L. and W. P. Shuman, "Asbestos for Reinforcing Plastics," <u>Plastics Design and Processing</u>, February 1967

Kimball, Kenneth E., <u>Effect of Thermal Shock Cycling on the Compressive Strength of Reinforced Plastic Laminates</u>, Final Report, TR-64-404, AD-466 642, US Department of Agriculture, Forest Products Laboratory, Madison, Wisconsin, May 1965

Kirk, R. B. and D. F. Othmer, editors, <u>Encyclopedia of Chemical Technology</u>, Volume II, Interscience Publishers, 1948, pp. 134-142

Lewis, Wayne C., <u>Thermal Conductivity — Temperature Relationship for Nine Glass and Asbestos Fiber-Reinforced Aircraft Plastics</u>, FPL Report 36, US Department of Agriculture, Forest Products Laboratory, Madison, Wisconsin, 1965

Long, F., B. B. Millwara, and R. J. Roberts, "Thermo-Oxidative Stability of Polyphenylene Resins in Asbestos Reinforced Laminates" (paper presented at the Tenth National Symposium of SAMPE, El Cortez Hotel, San Diego, California, 9 November 1966)

McGreevy, J. M., <u>Investigation of Class F Slot-Cell Composite, Natvar Corporation Isoglas — Unsaturated Asbestos Combination</u>, ML Project 5518-17-1, AD-269 610L, New York Naval Shipyard, Material Laboratory, Brooklyn, New York, 17 January 1962

Megson, N. J. L., "Structural Plastics for Airframe Construction" (paper presented at the Sixth Meeting of the Structures and Materials Panel, North Atlantic Treaty Organization Advisory Group for Aeronautical Research and Development, Paris, France, 4-8 November 1957)

Moore, B. J. C., <u>Friedel-Crafts Bonding Resins Prepared from Diphenoxydiphenylsilane</u>, Technical Report No. TR-65-259, AD-479 994, Royal Aircraft Establishment, Farnborough, England, November 1965

Moore, B. J. C., <u>Initial Evaluation of Asbestos Laminates Bonded with Polybenzyl Resin</u>, RAE-TN-CPM-46, Document N65-20744, Royal Aircraft Establishment, Farnborough, England, December 1963

Nagy, B. and T. F. Bates, "Stability of Chrysotile Asbestos," Amer. Mineral., 37, 1055-1058 (1952)

Nixon, B., Preliminary Investigation into the Physical Properties of Asbestos Laminates Bonded with a Terphenyl Resin, RAE-TN-CPM-8, AD-407 499, Royal Aircraft Establishment, Farnborough, England, February 1963

Nixon, B., Siloxane/Phosphate Resin Bonded Asbestos Laminates, AD-442 168, Royal Aircraft Establishment, Farnborough, England, April 1964

Nixon, B., Some Physical Properties of Terphenyl Resin Bonded Laminates, RAE-TN-CPM-47, Document N65-20662, Royal Aircraft Establishment, Farnborough, England, December 1963

Noble, T. Walter, "Interest in Non-Glass Reinforcements Grows," Plastics Design and Processing, June 1964, pp. 13-17

Pidgeon, L. M. and A. van Wissen, "The Adsorption of Water by Asbestos Fiber," Can. J. Res., 9, 155-158 (1953)

Pundsack, F. L., "The Properties of Asbestos. I. The Colloidal and Surface of Chrysotile," J. Phys. Chem., 59, 892 (1955)

Pundsack, F. L., "The Properties of Asbestos. II. The Density and Structure of Chrysotile," J. Phys. Chem., 60, 361 (1956)

Pundsack, F. L. and G. Reimschussel, "The Properties of Asbestos. III. Basicity of Chrysotile Suspensions," J. Phys. Chem., 60, 1218 (1956)

Rader, Charles A. and Anthony M. Schwartz, Colloidal Asbestos Fibrils as Reinforcements for Polymeric Structures, Final Report, Contract No. NASw-1420, Harris Research Laboratories, covering period 1 May 1966 to 30 April 1966; see also First Quarterly Progress Report (May-July 1966) and Third Quarterly Progress Report (November-January 1967), see also NASA Contractor Report NASA CR-893, September 1967.

Raphael, Thomas, "Predicting Service Life of Plastics," Plastics Technology, 26-28 (October 1962)

Rogers, K. F., Some Thermal Properties of Durestos Type Materials. Part II, RAE-TN-Chem-1358, AD 233-922, Royal Aircraft Establishment, Great Britain, November 1959

Rosato, D. V., Asbestos: Its Industrial Applications, Reinhold Publishing Company, 1959

Rosato, D. V., "Nonwoven Fibers in Reinforced Plastics," Industrial & Engineering Chemistry, 54 (8), August 1962

Schmidt, G. A., Whisker Matrix Bonding Studies, Final Report, AD-475 960, Contract NOw-64-0330-D, General Electric Company, Missile and Space Division, Philadelphia, Pennsylvania, May 1965; see also Quarterly Progress Report No. 3, March 1965

Schwartz, A. M., C. A. Rader, and Davis, The Reinforcement of Polymeric Structures by Asbestos Fibrils, Final Report, Contract NASw-1183, Harris Research Laboratories, Washington, D.C., April 1965 to 1966

Schwartz, Herbert S., Laboratory Techniques for Studying Thermally Ablative Plastics, ASD TR 61-517, AD-273 665, Nonmetallic Materials Laboratory, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, September 1961

Sterman, S. and J. G. Marsden, "Improved Thermosetting Systems," Plastics Technology 38-41 (May 1963)

Stevens, Gordon H., Effect of Thermal Cycling on Tensile and Compressive Strength of Reinforced Plastic Laminates, RP-FPL-37, AD-621 576, US Department of Agriculture, Forest Products Laboratory, Madison, Wisconsin, August 1965

Trainor, J., "Cushioned Warp-Polyimide Evaluation," Raybestos, Manhattan, New York (unpublished data)

Trenouth, J. M., The Propaedeutics of Natural, Synthetic, and Beneficiated Asbestos, Report MS-105, NRC Report 6248, AD-257 469, National Aeronautical Establishment, Canada, March 1961

Vondracek, C., Synthesis and Formulation of Inorganic Bonded Organic Fiber Reinforced Non-Metallic Structural Materials, ASD TDR-62-1107, AD-412 707, Contract AF 33(657)7587, Westinghouse Electric Corporation, Pittsburgh, Pennsylvania, January 1963; see also Quarterly Report No. 5, by C. H. Vondracek and L. E. Moberly (January-March 1963)

Wood, G., Temperature Limitations of Polymeric Materials; Part 2. Structural Reinforced Plastics, AD-443 634, Royal Aircraft Establishment, Farnborough, England, February 1964

Woodrooffe, H. M., "Pyrolysis of Chrysotile Asbestos Fiber," Can. Min. & Met. Bul., September 1956

Young, G. J. and F. H. Healey, The Physical Structure of Asbestos, Lehigh University, Surface Chemistry Laboratory, Bethlehem, Pennsylvania, October 1954

Young, G. J. and F. H. Healey, The Surface Properties of Chrysotile Asbestos, Lehigh University, Surface Chemistry Laboratory, Bethlehem, Pennsylvania, October 1954

79